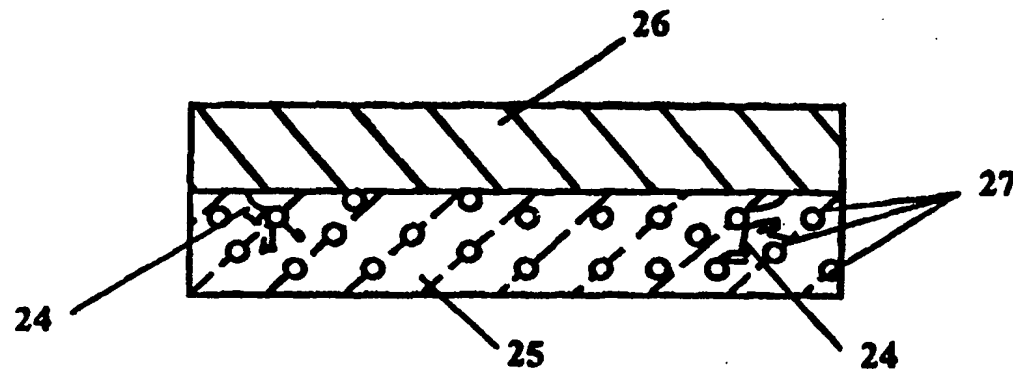


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B32B 3/00, 15/00, B21F , H01L 29/12</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/08672</b> <b>(43) International Publication Date:</b> 5 March 1998 (05.03.98)
<b>(21) International Application Number:</b> PCT/US97/14913 <b>(22) International Filing Date:</b> 25 August 1997 (25.08.97)  <b>(30) Priority Data:</b> 08/697,739 29 August 1996 (29.08.96) US  <b>(71)(72) Applicant and Inventor:</b> DeROCHEMONT, L., Pierre, doing business as C2 TECHNOLOGIES [US/US]; Complex 46, 37 Towle Farm Road, Hampton, NH 03843-0054 (US).  <b>(72) Inventor:</b> FARMER, Peter; C2 Technologies, P.O. Box 57, Hampton, NH 03842 (US).  <b>(74) Agents:</b> COHEN, Jerry et al.; Perkins, Smith & Cohen, One Beacon Street, Boston, MA 02108 (US).		<b>(81) Designated States:</b> AT, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METAL CERAMIC COMPOSITES WITH IMPROVED INTERFACIAL PROPERTIES    <b>(57) Abstract</b>  A metal-ceramic composite comprised of a metal member bonded to a ceramic oxide member through a covalent bond formed at temperatures less than 880 °C, and metal-ceramic composites that are so constructed as to control internal stress or increase crack-resistance within the ceramic member under applied thermal or mechanical loads to the composite, such composite with ferrite or alumina bonded sets of such metal-ceramic computers and end use devices including printed circuit boards, EMI shields and higher level assemblies including such devices.		

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**METAL CERAMIC COMPOSITES WITH IMPROVED INTERFACIAL PROPERTIES****CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims priority of U.S. Patent Application Serial No. 08/697,739 entitled METAL CERAMIC COMPOSITES WITH IMPROVED INTERFACIAL PROPERTIES AND METHODS TO MAKE SUCH COMPOSITES filed August 29, 1996.

**FIELD OF THE INVENTION**

The present invention relates generally to certain classes of metal-ceramic composites, and, more particularly, to structural and functional such composites and devices incorporating such composites, including, among others, printed circuit boards, EMI resistant panels and combined printed circuit boards/EMI resistant panel devices.

**BACKGROUND OF THE INVENTION**

Metal-ceramic composites comprising a metallic member bonded to a ceramic member have many useful applications in areas including, but not limited to, electronic circuits, engine components. In many of these applications the interface between the metal member and the ceramic member is subject to mechanical stress generated at, or close to, the interface formed between the metal and the ceramic. Preferred combinations of metallic

composition and ceramic composition often require an interface to be formed between a metallic composition and a ceramic composition that have poorly matched coefficients of thermal expansion. These metal-ceramic composite structures are unreliable as interfacial stresses develop between metal and ceramic members cause the composite to crack, deform, or delaminate as a result of operational heat cycling. Methods to economically construct metal-ceramic composites with improved interfacial properties, and the composites constructed therewith, are clearly desirable.

Electronic circuits, be they microelectronic circuitry contained or embedded on the surface of a semiconductor chip or an integrated circuit built on a circuit board, generate both heat and electromagnetic field emissions. The more powerful microelectronic circuits used in some of these devices generate significant levels of heat, which can compromise performance in metal ceramic composite circuit boards lacking efficient thermal management systems.

Thus, methods that can be widely applied to improve the performance of bulk metal-ceramic composites subjected to extreme linear expansions along at least one interface formed between the metal member and the ceramic member in metal-ceramic composite circuit boards, and bulk composites in general, are, therefore, also desirable.

The following patents are listed as examples of the prior art: Kashiba et al, U.S. Patent Nos. 5,153,077 and 5, 251,803; Komorita et al, U.S. Patent No. 5,155,665; Tanaka et al, U.S.

Patent Nos. 4,959,507 and 4,987,677; Ookouchi et al, U.S. Patent No. 4,981,761; Su et al, U.S. Patent No. 5,108,026; Simon et al, U.S. Patent No. 5,342,653. The publications of A. Goldman, in "Modern Ferrite Technology," Van Nostrand Rheinhold, New York, USA (1990) and A.J. Baden Fuller, in "Ferrites at Microwave Frequencies," Peter Peregrinus Ltd., London, U.K. (1987) provide reference literature on the physical properties of ferrite ceramics at low and microwave frequencies. Aspects of these references will be also described further in the Detailed Description of the present invention.

#### SUMMARY OF THE INVENTION

The method and products of the present invention overcome many of the problems associated with the production of past metal/ceramic components. The examples of the present invention stated below under "Detailed Description of Preferred Embodiments" are provided for illustrative purposes and not to limit the scope of the invention.

The invention involves deposition of a metal precursor to a ceramic composition (e.g. ceramic oxide such as  $\text{Al}_2\text{O}_3$  or other single or mixed oxides, borides, carbides, nitrides, silicides) on a metal substrate at a molecular level as a finely divided form of highly adherent metalorganic compounds followed by pyrolysis.

The overall process is conducted at low temperature and involves the method of metalorganic chemical spray pyrolysis. Using this method, metal precursors to the ceramic

oxide composition are introduced as metalorganic salt complexes, (i.e., metal complexes having organic ligands), into an organic solvent. Together they form the metalorganic precursor solution. High molecular weight carboxylic acid salts, such as 2-ethylhexanoates, or naphthenates, are the preferred metalorganic species using the process. In solution, the various ceramic precursors are mixed at the molecular level and thus, in minutes, achieve a state of ultrafine subdivision that typically is only achieved after calcining a slurry of powder precursors for many hours. Ceramic precursors are generally introduced into the metalorganic solution in concentrations in the range between 0.05% and 25% equivalent-weight oxide (eq.-wt%), although precursor concentrations in the range of 1% and 20% eq.-wt% are preferred. The spray conditions can be adjusted for compositional (and physical property) uniformity throughout the thickness of the eventual ceramic layer or for graded or otherwise differentiated composition and properties, e.g. graded coefficient of thermal expansion.

This state of ultrafine subdivision among the precursors is retained when the metalorganic solution is nebulized into an aerosol mist and deposited as a ceramic oxide (or the like) on the surface of a heated substrate. The substrate surface must be heated to a temperature that is greater than the boiling point of the organic solvent, which evaporates during ceramic deposition, and at least greater than the decomposition temperature of the

organic ligand that is most sensitive to thermal decomposition and contained in the metalorganic salt complex that, too, is most sensitive to thermal decomposition. It is preferred to heat the substrate to a temperature that is at least equivalent to the decomposition temperature of the organic ligand which is most sensitive to thermal decomposition and contained in the metalorganic complex which is least sensitive to thermal decomposition. Carboxylic acid salt precursors are preferred because of their low volatility.

During pyrolysis in an ambient oxygen atmosphere, the metalorganic precursors decompose into highly energetic metal radicals that rapidly seek to form covalent bonds with an unbound electron. Heated substrate surfaces comprise a sheet of dangling bonds that are also excited to form a lower energy bond with the metal radicals of the decomposing metalorganic salt complex. Metalorganic salt complexes typically decompose over a temperature range of 250-450° C. This process thus allows a covalent bond to be formed between the deposited ceramic material and a heated metal member at a low temperature in the range of 250-450° C. The deposited ceramic retains the state of ultrafine subdivision achieved in the metalorganic solution because the rapid pyrolysis of the precursor droplet, cooled by adiabatic expansion during aerosol nebulization, occurs at such a high rate that the mixed precursors have little or no time to segregate and sequentially decompose as individual metal oxide species.

The ceramic deposited on the heated metal substrate is initially porous and comprised of a solid solution with randomly oriented crystalline structure. The deposited ceramic member can be brought into a physical state comprised of highly oriented and densely packed crystalline grain structure using multiple short duration sequential reaction and mechanical pressurization processing steps. The density of ceramic so-processed can achieve levels approaching 97% and preferably, for many applications over 99% of theoretical density.

For example, one aspect of the present invention provides for the dispersion of secondary phase material particles in a ceramic medium in order to increase the crack resistance of the ceramic medium.

Another feature of the present invention provides for a thermally insulating ceramic member to be deposited on the metal member by spray pyrolyzing a solution of metalorganic precursors and thus permits the composition of the ceramic member to be altered by adjusting the precursor concentration of the metalorganic solution with the thickness of the deposited ceramic. This reduces shear stress in a ceramic member of a thermally loaded metal-ceramic composite by introducing, as stated above, a composition profile in the ceramic member bonded to the metal member in order to produce a gradient in the coefficient-of-thermal-expansion within the ceramic member in a manner that reduces shear stress in the ceramic member.



The present invention, by virtue of being a low-temperature manufacturing process, also represents a further improvement over the prior art because it allows a far greater selection of constraining metal members than the prior art. Further, the ability to form a covalent bond between the deposited ceramic member and the metallic substrate without a molten bonding agent or adhesive, as is enabled under the present invention, permits even greater improvement over the prior art by introducing stress-reducing micro-mechanical elements to the ceramic layer throughout in the thickness and/or near the metal-ceramic interface, such elements substantially retaining their compositional and physical integrity.

Another particular aspect of the metal-ceramic composites of this invention relates to the use of the metal-ceramic composites as a metal-ceramic composite substrate for printed circuit boards. Also under the present invention, high conductivity metal-alumina-high conductivity metal, such as copper-alumina-copper structures, with improved crack-resistance and interfacial properties are produced by depositing an alumina-based ceramic on the high conductivity metal member.

Another particular effect of the invention relates to the production of EMI resistant panels or combinations of EMI resistant panels/printed circuit boards.

In making complete metal-ceramic-metal printed circuit boards, it is preferred to separately produce single metal-ceramic composites and bond them, ceramic face to

ceramic face, with heat/pressure assisted self bonding or via an intermediate layer.

Under certain processing conditions, the surface texture of one or both the ceramic-faces of metal-ceramic composites bonded together ceramic-face to ceramic-face can become grossly undulated. Surfaces with controlled roughness will generally produce better bonding. It is recommended, but not strictly necessary, to produce a ceramic-face bonding surface that has a mean surface roughness of 25-50 microns, and a maximum surface roughness of 40-100 microns. Ground surfaces with controlled surface roughness can be produced using a variety of techniques, such as abrasion blasting, that are well known to practitioners skilled in relevant art.

EMI resistant panels mentioned above involve use of ferrite ceramics, e.g.  $\text{PbO} + \text{Fe}_2\text{O}_3 \Rightarrow \text{PbFe}_2\text{O}_4$  of spinel or inverse spinel crystallographic structures. The ferrite grains are grown to over 2.5 micron size (usually anisotropic) preferably 10 to 30 micron size in most applications to enhance EMI absorption.

For a better understanding of the present invention, together with other and further objects, reference is made to the following description taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional representation of a metal-ceramic composite printed circuit board as found in the prior art;

FIG. 2. represents a cross-sectional view of a typical fracture pattern for a metal-ceramic composite interface that has been thermally over-stressed in a typical printed circuit board as shown in FIG. 1;

FIG. 3 represents a cross-sectional view of a metal-ceramic composite of the preferred embodiments of the present invention wherein particles of at least one secondary phase material are dispersed in the composite's ceramic member to impede crack propagation and increase crack-resistance;

FIG. 4 represents a schematic cross-sectional view of the coefficient of thermal expansion within a ceramic member;

FIGS. 5 (a), (b) and (c) depict various positions of a constraining metal member within the composite of an embodiment of the present invention;

FIG. 6 (a) is a cross sectional view of a metal ceramic structure;

FIGS. 6 (b) and 6 (c) represent a model that visually simulates the thermal deformation in a metal-ceramic composite substrate printed circuit board and compares thermal deformation in the composite when the mounting area contains a molybdenum constraining-metal member to the thermal deformation in the composite when the mounting area contains a titanium constraining-metal member.

FIGS. 7 (a)-(d) depict cross-sectional views of the construction of a metal-ceramic composite in which adhesion-resistant bodies are placed on a metal member substrate (a), or coated with an epoxy resin before being attached to the metal

member substrate (b), a ceramic member is deposited on both the adhesion-resistant bodies and the metal member substrate (c), and the resin epoxy is finally removed (d);

FIGS. 8 (a) and (b) show the top perspective of various shapes and forms for adhesion-resistant bodies;

FIGS. 9 (a) and (b) depict various parameters that define a micro-mechanical strut at a metal-ceramic oxide interface (a) and the flexure the micro-mechanical struts provide to the ceramic at the interface (b);

FIG. 10 shows the characteristic stress-reduction versus the depth of micro-mechanical struts formed in the ceramic member at various distances from the metal-ceramic interface;

FIG. 11 shows the characteristic stress-reduction versus the width of micro-mechanical struts formed in the ceramic member at various distances from the metal-ceramic interface;

FIG. 12 depicts low-field losses characteristic to ferrite ceramics;

FIGS. 13 and 14(a) and (b) depict metal-ceramic composite substrates for printed circuit applications; and

FIGS. 15(a) and (b) and 16 and depict metal-ceramic composites with a ferrite ceramic attached to one major surface of the structure.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The following brief analysis is provided in order to better understand the present invention. In addition, a number of terms used

throughout this description are also provided below.

The term "ultrafine subdivision" is understood to represent a ceramic whose precursors have been mixed at the molecular level, as in a solution, as opposed to a ceramic whose precursors were mixed as particulates with a definitive particle size, as in a slurry. The term "secondary phase material" is understood to represent a compositional state of matter dispersed in a ceramic deposited or formed on a metal member, such that the "secondary phase material" is characterized by an elemental composition, material phase, or crystallographic structure that is different from the deposited ceramic into which it is dispersed. The "secondary phase material" may be a single crystalline phase, a ceramic phase, a glass phase, graphite, a metal phase, a shape-memory alloy phase, or any composite form of said material phases that produces a Young's modulus that is less than the Young's modulus of the ceramic medium into the "secondary phase material" has been dispersed. The term "shape-memory alloy" is understood to represent a metallic phase or glassy metallic phase that exhibits superior ductile properties under mechanical stress and the ability to return to its initial geometric shape and physical dimensions exhibited in an unstressed state after the application of said mechanical stress has been relieved.

Composite bodies that comprise a ceramic member contacted to a metallic member can significantly improve the performance of a conventional non-composite part over a wide

range of applications. In practice, however, unless special measures are taken to engineer a proper interface between the ceramic member and the metal member, the functionality of the composite bodies can be extremely limited as the intended applications often subject the composite bodies to thermal loads or mechanical stress that cause the metal and ceramic members to become mutually incompatible in a single composite body. Metals and ceramics are essentially characterized by starkly different chemical, mechanical and thermal properties. Metals are, typically, characterized by ductile properties that permit them to elastically flex and accommodate a higher degree of mechanical stress prior to reaching a point inelastic fracture. Metals, typically, exhibit thermal conductivities that are superior to those common to most ceramics. Ceramics, typically, are characterized by rigid mechanical properties that allow them to resist flexure, however, this brittle nature can make the ceramic more susceptible to inelastic fracture under equivalent mechanical loads. A composite body, comprised of a metal member bonded to a ceramic member can blend the superior properties of each member to improve device performance in a variety of applications.

The ultimate performance in such a composite body will, in many instances, be determined by stresses generated at, or close to, the interface between the ceramic member and the metallic member, where the disparate thermal and mechanical properties of one member will oppose the other member's natural response to an applied thermal or mechanical

load beyond its natural ability to do so. An example of a failure mode in a metal-ceramic composite body is easily demonstrated when a typical composite body is subject to strong variations in temperature, and/or large temperature differential across the composite body itself, and the metal-ceramic interface in particular. Under such circumstances, applications failure typically relates to interfacial stress caused by the mismatch in the coefficients of thermal expansion between the ceramic member and the metal member. When both members are restrained at the interface, a simple expression, using the product of the Young's modulus,  $E$ , [ $E = \text{Newtons/mm}^2$ ], the coefficient-of-thermal-expansion,  $\alpha$  [ $\alpha = \text{K}^{-1} (\text{in.}(\text{cm})/\text{in.}(\text{cm})\text{-}^\circ\text{K})$ ], and the temperature differential to which  $\Delta T$ , [ $\Delta T = \text{K}$ ], can be used to assess the thermal dependence of interfacial stress,  $\Delta S$ :

$$\Delta S = KE\alpha_{\text{ceramic}}\Delta T \quad (1)$$

where,

$$K = (1 - \alpha_{\text{metal}}\Delta T_{\text{metal}}/\alpha_{\text{ceramic}}\Delta T_{\text{ceramic}})/(1 + A_{\text{ceramic}}E_{\text{ceramic}}/A_{\text{metal}}E_{\text{metal}}) \quad (1a)$$

and,  $A$  represents the area of the subscripted member.

It is straightforward to evaluate the thermal incompatibility of pertinent metal-ceramic composite bodies. For instance, as shown in FIG. 1 of the drawings, printed circuit boards for high power semiconductor integrated circuits ("SIC's") generally comprise a metal-ceramic composite substrate consisting of a low-cost, high thermal conductivity, high

electrical conductivity metal sheet 1A bonded to a low-cost, low-dielectric constant, low thermal conductivity ceramic 2 on one major surface of the ceramic, with another low-cost, high thermal conductivity, high electrical conductivity metal sheet 1B bonded to the ceramic's opposing major surface. In the printed circuit board application, the metal sheet 1A will be etched to form a network of mounting areas 1C, onto which semiconductor integrated circuits 3 are mounted, and electrode areas 1D, that are used to transport electrical signals across the surface of the printed circuit board. Aluminum wire 4 is ultrasonically bonded between the SIC 3 and the electrode area 1D to electrically connect the semiconductor chip to the electrode network on the surface of the printed circuit board. Prior art has typically used aluminum oxide (alumina) as the ceramic member 2 and copper as the metal sheets 1A and 1B, although it is possible to use other metals and ceramics, such as non-oxide ceramics, to form the printed circuit board structures. Copper has a coefficient-of-thermal-expansion of  $\alpha_{\text{copper}} = 16.5 \times 10^{-6} \text{ K}^{-1}$ , and a Young's modulus of  $E_{\text{copper}} = 11 \times 10^4 \text{ (Newtons)/mm}^2$ , whereas the coefficient-of-thermal-expansion for alumina ceramic is  $\alpha_{\text{ceramic}} = 8.8 \times 10^{-6} \text{ K}^{-1}$ , and it has a Young's modulus of  $E_{\text{ceramic}} = 160\text{-}300 \text{ (Newtons)/mm}^2$ . Using equation (1), it is straightforward to determine that approximately 2 megapascals (MPa) of stress will be generated for each degree of rise and fall in temperature at the interface formed when alumina ceramic is directly bonded to copper



metal. This means that a 10-15° K (°C) rise or fall in temperature will bring the alumina ceramic to a point of internal fracture. FIG. 2 shows a fracture pattern that is typical of an over-stressed interface, comprising cracks 5 in the ceramic member 6 that is bonded to the metal member 7. Semiconductor integrated circuits are generally required to operate reliably over temperatures ranging from -40 °C to 150 °C. It is, therefore, essential that the metal-ceramic composite, when used as a printed circuit board substrate on which SIC's are mounted, have reliable function over an identical range of temperatures. Simple metal-ceramic composite structures, wherein metals having a coefficient-of-thermal-expansion comparable to that of copper are directly bonded to the ceramic member are not sufficient to satisfy these requirements.

In order to achieve reliable function as a printed circuit board, it is also necessary that the metal member on which semiconductor integrated circuits are mounted satisfy other physical tolerances related to surface roughness and Vickers hardness. Tanaka *et al.* disclose, in U.S. Patents Nos. 4,959,507 and 4,987,677, that the unit failure rate of metal-ceramic composite substrate circuit boards, wherein the composite substrate circuit boards comprise copper sheets bonded through the eutectic bonding process to the opposing major surfaces of a ceramic member, can be reduced if surface roughness of the copper sheet of the metal-ceramic composite onto which electronic circuits are mounted has a median surface roughness not greater than 3

microns and a maximum surface roughness not greater than 18 microns. Although, the specifications for surface roughness are sufficient, copper members having median surface roughness not greater than 1 micron and a maximum surface roughness not greater than 8 microns are preferred. The reduced surface roughness improves the quality of a solder bond between the semiconductor integrated circuit and the metal surface comprising the mounting area of the metal-ceramic composite substrate onto which it is mounted. Komorita *et al.* (U.S. Patent No. 5,155,665) disclose that the unit failure rate of metal-ceramic composite substrate circuit boards, wherein the composite substrate circuit boards comprise copper sheets with the copper sheets bonded through the eutectic bonding process to the opposing major surfaces of a ceramic member, can be reduced if the Vickers hardness of the copper sheet onto which microelectronic circuits are eventually mounted lies in the range of 40 Kg/mm<sup>2</sup> to 100 Kg/mm<sup>2</sup>. Aluminum wire that is ultrasonically bonded to copper sheets with a Vickers hardness less than 40 Kg/mm<sup>2</sup> is prone to rupture in the vicinity of the bond, as the ultrasonic energy used in the bonding process is sufficient to bury the wire into the soft copper sheet and catastrophically elongate the aluminum wire. An ultrasonic bond formed between aluminum wire and a copper sheet with a Vickers hardness greater than 100 Kg/mm<sup>2</sup> frequently has poor adhesion as the ultrasonic wave is attenuated in the hard copper sheet. Metal-ceramic composite substrates that

have copper mounting areas with a Vickers hardness in the range between 60 Kg/mm<sup>2</sup> to 80 Kg/mm<sup>2</sup> are preferred in printed circuit board applications.

Interfacial stress at a metal-ceramic composite interface can be reduced if the metal member bonded to the interface contains a constraining-metal member which acts to restrain the linear thermal expansion of the metal member. Kashiba *et al.*, describes in U.S. Patent Nos. 5,153,077 and 5,251,803 the use of a constraining-metal member integrally-bonded into a metal-ceramic composite substrate, wherein the constraining-metal member reduces thermally-generated mechanical stress at the interface between metal and ceramic members in the composite structure, or between the metal layer and a semiconductor integrated circuit mounted on the metal member. In addition to having a lower coefficient-of-thermal-expansion, the constraining-metal layer must have a higher yield strength than the copper sheet to which it is bonded. Copper has a yield strength of 10 Kg/mm<sup>2</sup>, whereas molybdenum, a suitable constraining-metal member, has a yield strength of 50 Kg/mm<sup>2</sup>. The ductile copper, restrained by the constraining-metal member, will not crack as its elastic properties absorb the stress generated by linear expansions at the copper-constraining-metal interface during thermal cycling. The ceramic member in such a metal-ceramic composite structure is subject to a reduced level of mechanical stress as thermally generated linear expansions of the modified metal member are determined by the

constraining-metal member's coefficient-of-thermal-expansion. Thus, a constraining-metal modified metal-ceramic composite comprising an alumina ceramic,  $\alpha_{\text{ceramic}} = 8.8 \times 10^{-6} \text{ K}^{-1}$  and  $E_{\text{ceramic}} = 160\text{-}300 \text{ N/mm}^2$ , and molybdenum as the constraining-metal member,  $\alpha_{\text{molybdenum}} = 5.43 \times 10^{-6} \text{ K}^{-1}$  and  $E_{\text{molybdenum}} = 33.1 \times 10^4 \text{ N/mm}^2$ , will experience 0.7 MPa of stress for each degree of rise and fall in temperature, according to equation (1). This means that a 30-45 K ( $^{\circ}\text{C}$ ) rise or fall in temperature will bring the alumina ceramic to a point of internal fracture. While this represents a substantial improvement over metal-ceramic composites that do not contain constraining-metal layers, improvements upon the prior art are clearly desirable for semiconductor applications, as well as other applications in which the metal-ceramic composite is subjected to even greater thermal or mechanical loads.

The present invention provides methods to improve the thermal and mechanical integrity of metal-ceramic composites that have at least one interface in which the composite's metal member is directly bonded to the ceramic member. These improvements to the prior art relate specifically to the construction methods used to assemble the metal-ceramic composite. Additionally, the present invention improves the interfacial properties and fracture mechanics of metal-ceramic composites by allowing more fracture-resistant forms of alumina ceramic to be assembled into the composite and by adding micro-mechanical features to the bonding

surface of the ceramic member in contact with the metal member that increase the flexure of the ceramic member in response to linear expansions or contractions of the metal member. The present invention also introduces methods to control the fracture mechanics of the interface.

Another significant attribute of the present invention is that it allows the metal-ceramic composite to be formed at much lower processing temperatures. Prior art construction methods utilize pre-fabricated ceramic and metal members that are bonded together using processing techniques that subject the metal-ceramic composite to temperatures at least in excess of 900 °C. It is well known to practitioners skilled in the art of heat-treating sheet metal that prolonged exposure to elevated temperatures close to the melting point of the metal sheet, i.e., within 200 °C of its melting point, will reduce its hardness. The degree to which the hardness is reduced is a function of both the temperature as well as the time period over which the metal sheet is exposed to the elevated temperature. Increasing the time period over which the metal is exposed to an elevated temperature sufficient to soften the metal will proportionally reduce its hardness.

The present invention further improves upon the prior art by being a low-temperature process and one that can be suitably engineered for continuous production. These processing features not only impact the ease with which metal-ceramic composites can be produced, they also increase the economy of industrial

production. Methods detailed in the prior art represent batch production techniques, in which production units are produced in units of one, or multiples of one depending on batch size. This means all the component parts to the finished product need to be prepared to unit size prior to assembling the final product. Batch production methods are less efficient because they generally represent multiple processing and quality assurance steps for each of the components during sub-assembly prior to forming the finished good in final assembly. Continuous production methods improve the economy of an industrial process by reducing the number of processing steps and increasing production rate. As detailed below, the present invention can be easily engineered into a continuous process. Metal-ceramic composite substrates for printed circuit board applications are easily assembled by rolling copper sheet into a deposition chamber where a layer of alumina ceramic is spray-pyrolyzed onto its surface to form a sheet comprising a metal layer bonded to a ceramic layer. Two such sheets, or one sheet folded onto itself, are joined through a mechanical swaging step, ceramic face to ceramic face, to form the metal-ceramic-metal composite substrate structure. Finished products are then stamped out of a continuously processed sheet. By virtue of the present invention comprising a low-temperature continuous process, it is not necessary to start with excessively hardened copper sheets to achieve metal-ceramic composite substrates in which the copper mounting and electrode areas

satisfy hardness tolerances necessary to produce a reliable printed circuit board. Since all the bonding steps utilized under the present invention can be realized at temperatures below 900°C, hardness reduction during subsequent annealing steps is mitigated by lower temperature processing, providing more control over the Vickers hardness of the metal members in the finished composite.

An essential feature of the present invention is that it allows a ceramic member to be bonded to any metal member, irrespective of metal and ceramic composition(s), through a covalent bond formed using processing temperatures that can be less than 500°C. More specifically, ceramic oxide is bonded to metal at low-temperature by the method of metalorganic chemical spray pyrolysis. Using this method, metal precursors to the ceramic oxide composition are introduced as metalorganic salt complexes, (i.e., metal complexes having organic ligands), into an organic solvent. Together, they form the metalorganic precursor solution.

A distinguishing characteristic of metal-ceramic composites manufactured using the metalorganic spray pyrolysis process is that a direct rigid bond is formed between the metal and the ceramic members without the use of an adhesive or bonding agent that comprises a compositional state of matter that is different from the ceramic and the metal member, such as is the case when a solder material or a eutectic material is used to form the bond. By virtue of covalent bonding between the metal and the ceramic members, a compositional profile of the

metal-ceramic interface is characterized by an abrupt termination of the metal composition and an equally abrupt beginning of the ceramic composition. These interfaces do not contain a formerly liquid phase material that has been solidified into a layer many tens of microns thick to form the bond. As will be shown below, this method of forming a "*clean*" interface now makes it possible to engineer micro-mechanical features bonded to the ceramic, but not to the metal, that enhance the interfacial properties of the composite body.

One aspect of the present invention, shown in FIG. 3, is the incorporation of secondary phase material particles dispersed in a ceramic medium. For example, a crack 24 propagating through a brittle ceramic medium 25 that has been generated by stresses at the interface between the brittle ceramic medium 25 and a metal member 26 will be deflected or have its energy partially absorbed when it encounters the secondary phase material particles 27 dispersed in the brittle ceramic medium. As a result, the secondary phase material particles dispersed throughout a brittle medium increase the crack resistance of the brittle medium. The fracture mechanics of a composite body can also be improved if the composite body is formed in a manner that allows thermally compressive forces to pre-stress the composite body in a manner that opposes, much as is the case with a pre-stressed bolt, the thermal and mechanical loads anticipated from an intended application. Similarly, interfacial stress between a high thermal expansion coefficient metal and a lower



thermal expansion coefficient ceramic can be reduced by modifying the Young's modulus of the high thermal expansion coefficient metal. Suitable modifications to the high thermal expansion coefficient metal would include perforating the high thermal expansion coefficient metal or by making it porous. As set forth below, the present invention allows any, or all, of these improvements now to be incorporated into the construction of metal-ceramic composite bodies.

A metal-ceramic composite with improved interfacial properties according to this invention can be manufactured as follows:

Specifically, the present invention utilizes a method to produce a metal-ceramic composite in which the ceramic member forms a covalent bond with the metal member by the method of metalorganic spray pyrolysis. The ceramic member consists of a primary ceramic medium with ultrafine subdivision that has been formed on the metal member from a spray pyrolyzed metalorganic solution, and the ceramic member contains a dispersion of previously formed particles of secondary phase materials that increase the crack resistance in the ceramic member. The particles of secondary phase materials are dispersed in the ceramic medium by forming a colloidal suspension of the secondary phase materials in the metalorganic solution prior to spray pyrolyzing the metalorganic solution containing a colloidal suspension of the secondary phase material particles on the metal member of the metal-ceramic composite. The metalorganic precursors

are pyrolyzed into oxide ceramic on the metal member substrate heated to temperatures typically greater than 250°C, and typically less than 500°C. This range of temperatures is generally insufficient to dissolve the secondary phase material particles 27 into the ceramic medium 25. As a result, particles 27 of secondary phase materials dispersed throughout the metalorganic solution become dispersed, as secondary phase material particles, in the spray pyrolyzed ceramic. It is a preferred embodiment of this invention to use particulates of secondary phase materials that are characterized as having intrinsic mechanical properties that are less brittle, i.e., has a lower Young's modulus, than the ceramic medium 25 formed around them by the pyrolyzed metalorganic precursor solution. The secondary phase material particles 27 may comprise a metal or metal alloy, a glass phase, a shape memory alloy, graphite, an oxide or non-oxide material, or a crystalline ceramic or single crystal material phase.

This particular aspect of the invention has special significance for alumina-based ( $\text{Al}_2\text{O}_3$ -based) ceramic members on metal substrates. As mentioned above, the prior art instructs on the construction of metal-ceramic composites formed by bonding a previously formed ceramic member (i.e., a ceramic member that already has been sintered, cut, and polished) to metal sheets. Alumina represents one of the most highly refractory oxide ceramics. It liquefies at temperatures above 2054°C, and forms a partial liquid phase suitable for sintering at

temperatures above 1828°C. Given these highly refractory properties, it is exceedingly difficult to disperse particles of a mechanically "softer" secondary phase material within a solid solution of alumina ceramic without completely dissolving the secondary phase material particles completely into a ceramic formed from sinter-reacted powders. The present invention allows a colloidal suspension of secondary phase material particles to be dispersed throughout a solid solution of ceramic that is spray pyrolyzed around the secondary phase material particles at temperatures well below 1828 °C. The spray pyrolyzed ceramic may be crystallized and textured using a repetitive sequence of incremental reaction and mechanical swaging steps. During the formation of metal-ceramic composites that comprise a ceramic member possessing a thermal reaction temperature in excess of the melting temperature of the metal member to which it is bonded, it is preferred to utilize electromagnetic radiation to react and crystallize the ceramic member. In this embodiment a beam of electromagnetic radiation, characterized by an electromagnetic energy that is either in the microwave frequency spectrum or in the infrared frequency spectrum, can be directed onto the ceramic member to advance its state of crystallization. Simultaneously, the metal member, which is not irradiated by a suitably directed electromagnetic beam, can be held to a temperature well below its melting point. It is now well known to practitioners skilled in the art of microwave annealing of ceramic and other materials, that

certain frequencies of radiation will preferentially react certain chemical species of the irradiated material. It is a preferred embodiment of this invention to utilize a microwave frequency that induces strong crystallization in the alumina ceramic, but induces only a mild reaction with the secondary phase materials particles. The secondary phase material particles may have spheroidal dimensions ranging between 0.05 microns and 500 microns. Secondary phase materials particles with spheroidal dimensions less than 0.05 microns will have a tendency to be dissolved into the ceramic medium into which they have been dispersed during reaction treatments. Secondary phase material particles with spheroidal dimensions greater than 500 microns are so large that their intrinsic material properties have a tendency to dominate over the material properties of the ceramic medium into which they have been dispersed. A preferred embodiment of the present invention utilizes the secondary phase material particles having spheroidal dimensions in the range between 0.10 and 50 microns.

It is often desirable to form a metal-ceramic composite comprising a metal member having a coefficient-of-thermal-expansion that is significantly greater than the coefficient-of-thermal-expansion of the ceramic member. As mentioned above, the thermal performance of the metal-ceramic composite composed of metal and ceramic members having incompatible coefficients of thermal expansion can be improved if the ceramic member in the metal-

ceramic composite is maintained in a state of compressive stress over the range of temperatures at which the metal-ceramic composite is expected to operate. Such a state can be achieved if the metal member in the metal-ceramic composite is heated to a temperature that is greater than, or nearly equal to, the maximum temperature to which the pre-stressed metal-ceramic composite is expected to reach during an operational cycle prior to depositing the ceramic member on the metal member. It is a preferred embodiment of this invention to maintain the metal member and the deposited ceramic member at the elevated temperature until the pre-stressed metal-ceramic composite is fully constructed. Upon cooling to room temperature, the metal member in the pre-stressed metal-ceramic composite will contract to a much greater degree than the ceramic member, leaving the ceramic member in a state of compressive stress.

Furthermore, since the metal-ceramic composite is produced by depositing the ceramic member on the metal member, the present invention provides other means to manipulate the stress response of the ceramic to steady-state thermal loads that induce a temperature differential across the deposited ceramic member. For instance, a heat shield, manufactured by bonding a high thermal conductivity metal sheet to a thermally insulating ceramic on one major surface and exposing the opposing major surface of the metal sheet to a heat source, can be used to diffuse heat to heat sinks located at the minor

surfaces of the high thermal conductivity metal sheet, thereby impeding heat flow through the major surface at which the thermally insulating ceramic is bonded. Under steady-state conditions, the temperature of the thermally insulating ceramic member will be elevated to a higher temperature on the major surface at which it is bonded to the thermally conducting metal member, and be reduced to a lower temperature on its opposing major surface. As a consequence of this temperature profile across the thermally insulating member, the thermally insulating ceramic member will linearly expand to a greater degree at the major surface where it is bonded to the high thermal conductivity metal, and will linearly expand to a lesser degree if the thermally insulating ceramic member has uniform composition and an uniform coefficient-of-thermal-expansion. This difference in linear expansion produces a shear stress within the thermally insulating ceramic member having uniform coefficient of thermal coefficient. Under the present invention, the thermally insulating ceramic member is deposited on the metal member by spray pyrolyzing a solution of metalorganic precursors. The invention permits the composition of the ceramic member to be altered by adjusting the precursor concentration of the metalorganic solution with the thickness of the deposited ceramic. As shown graphically in FIG. 4, it is, thus, another preferred embodiment of the present invention to reduce shear stress in a ceramic member of a thermally loaded metal-ceramic composite by introducing a composition

profile in the ceramic member 19 bonded to the metal member 20, to produce a gradient in the coefficient-of-thermal-expansion within the ceramic member in a manner that reduces shear stress in the ceramic member.

Another aspect of this invention is to reduce the Young's modulus or the effective coefficient-of-thermal-expansion of the metal member in the metal-ceramic composite having metal and ceramic members with incompatible coefficients of thermal expansion. It is a preferred embodiment of this invention to reduce the Young's modulus of the metal member having a coefficient-of-thermal-expansion that is significantly greater than the coefficient-of-thermal-expansion of the ceramic member to which it is bonded by drilling holes in the metal member. These holes can be drilled prior to forming the ceramic on the perforated metal member, or after the metal-ceramic composite has been formed by means of conventional press drilling or laser drilling.

It is also a preferred embodiment of this invention to reduce the effective linear expansion of the metal member having a coefficient-of-thermal-expansion that is significantly greater than the coefficient-of-thermal-expansion of the ceramic member to which it is bonded in the metal-ceramic composite, by incorporating a constraining-metal member 28 into the metal member as shown in FIGS. 5 (a), (b) and (c), such that the constraining-metal member 28 incorporated into the metal member has a thickness that is  $\frac{1}{20}$ th to  $\frac{1}{3}$ rd the thickness of the metal member

having a high coefficient-of-thermal-expansion. The constraining-metal member 28 may be situated such that it is bonded on one major surface to the deposited ceramic member 29, and bonded to the high coefficient-of-thermal-expansion metal member 30A on its other major surface as diagrammed in FIG. 5(a). The constraining-metal member 28 also may be situated such that it is bonded on one major surface to the high coefficient-of-thermal-expansion metal member 30B, and the high coefficient-of-thermal-expansion metal member 30B is bonded to the deposited ceramic member 29 on its other major surface as diagrammed in FIG. 5(b). Alternatively, the constraining-metal member 28 may be situated such that it is bonded on one major surface to a high coefficient-of-thermal-expansion metal member 30A', and is bonded to another high coefficient-of-thermal-expansion metal member 30B' on its other major surface, with the other high coefficient-of-thermal-expansion metal member 30B' bonded to the deposited ceramic member 29 on its other major surface as diagrammed in FIG. 5(c).

The present invention, by virtue of being a low-temperature manufacturing process, represents a further improvement over the prior art because it allows a far greater selection of high coefficient-of-thermal-expansion metal member bonded to constraining-metal member combinations to be constructed. Furthermore, in many applications for metal-ceramic composites it is desirable to couple a high thermal conductivity and/or electrical conductivity metal



member to a thermally insulating and/or electrically insulating ceramic member. This is particularly true for metal-ceramic composites used as substrates in printed circuit board applications. In such instances, semiconductor integrated circuit elements are mounted on a metal member of the metal-ceramic composite substrate. The metal member is used to transport electrical current and also is used to dissipate heat generated by the SIC. In such applications it is particularly useful for the metal member to maximally dissipate heat and transport maximum levels of electrical current. As shown in Table I, metals that exhibit higher electrical and thermal conductivities commonly exhibit higher coefficients of thermal expansion, whereas metals with high yield strengths and low coefficients of thermal expansion, which are suitable for use as a constraining-metal member, typically exhibit poorer electrical and thermal conductivities. In order to achieve maximal operating performance in the printed circuit applications, it is preferable to configure the metal-ceramic composite with the constraining-metal member bonded between the ceramic member and the high thermal conductivity and/or high electrical conductivity metal member as shown in FIG. 6(a). It is straightforward to ascertain that the constraining-metal member in configurations of metal-ceramic composites such as those depicted in FIGS. 6(b),(c) will hinder the transport of electrical current to and from, or the dissipation of heat from, a semiconductor integrated circuit mounted on the exposed major surface of the

metal member. However, in many practical applications it is preferable to utilize the less optimal configuration shown in FIG. 6(c) when the thermal expansion of, and stress distribution in, the metal-ceramic composite during an operational cycle is considered. These points are most clearly demonstrated using computer simulations that visually plot the stress distributions and mechanical deformation which results when a given composite design is subjected to a thermal load typical of an operational cycle.

TABLE I

Material	Electrical Resistivity ( $\Omega\cdot\text{m}$ )	Thermal Conductivity ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )	Coefficient of Thermal Expansion ( $10^{-4}\text{K}^{-1}$ )
<b>Conducting Metal</b>			
Aluminum	$2.65 \times 10^{-8}$	237	23.03
Copper	$1.67 \times 10^{-8}$	401	16.5
Silver	$1.59 \times 10^{-8}$	429	19.2
Gold	$2.35 \times 10^{-8}$	317	14.2
<b>Constraining Metal</b>			
Antimony	$39 \times 10^{-8}$	243	8.5
Chromium	$12.7 \times 10^{-8}$	93.7	8.5
Iridium	$5.3 \times 10^{-8}$	147	6.2
Molybdenum	$5.2 \times 10^{-8}$	138	5.43
Tantalum	$12.45 \times 10^{-8}$	57.5	6.6
Tin ( $\alpha$ -phase)	$11.0 \times 10^{-8}$	66.6	5.34
Titanium	$42.0 \times 10^{-8}$	21.9	8.33
Tungsten	$5.65 \times 10^{-8}$	174	4.59
Vanadium	$24.8 \times 10^{-8}$	30.7	8.3
<b>Ceramic</b>			
Alumina	$10^{-10}$	0.42	8.8
Ferrite	$4 \times 10^{-1} - 10^{-10}$	4.0	7-10

TABLE I (CONTINUED)

Material	Poisson Ratio	Elastic Shear Modulus (GPa)	Elastic Tensile Modulus (GPa)	Hardness
<b>Conducting Metal</b>				
Aluminum	0.40	25	62	200 HV
Copper	0.343	46.8	125	37 HRB
Silver	0.37	46.3	125	25 HV
Gold	---	---	378	---
<b>Constraining Metal</b>				
Antimony	0.25	19	77.7	---
Chromium	---	---	154	---
Iridium	0.26	0.21	1.2	200 HV
Molybdenum	0.307	107	350	---
Tantalum	0.35	69	186	120 HV
Tin ( $\alpha$ -phase)	0.33	13.7	41.6	---
Titanium	0.34	80	235	70 HB
Tungsten	0.28	155	400	150 HV
Vanadium	0.36	46.4	130	70 HB
<b>Ceramic</b>				
Alumina	---	---	0.04	---
Ferrite	---	36	0.02	6 (Mohs)

FIG. 7 depicts magnified views of the structural response in 2 different configurations for metal-ceramic composite substrates in typical printed circuit board applications as simulated by finite element method ("FEM") analysis. The FEM analysis presented assumes the metal-ceramic composite structure sketched in FIG. 6(a). As shown on FIG. 6(a) the FEM model consists of a 150 °C heat source 31 to represent an SIC, and has heat sinking cooling fins 32 at the edge of a 3.00 mm thick copper mounting area 33, which is bonded to a 0.45 mm thick constraining-metal member 34. The constraining-metal member 34 is bonded through its opposing major surface to a 1.00 mm alumina ceramic member 35, which, in turn, is bonded through its opposing major surface to a 0.30 mm thick copper ground plane member 36. The model further assumes the materials properties for alumina, copper, molybdenum and titanium as tabulated in Table I. The outer edges of the model (including the cooling fins) are subject to an environmental load of 27 °C and convective heat loss of  $4.33 \times 10^{-6}$  W/mm<sup>2</sup>. The system has been allowed to relax to its steady-state equilibrium values to simulate conditions of maximal thermal loading.

FIG. 6(b) depicts a magnified view (20x) of the FEM-simulated deformation to the metal-ceramic composite when the constraining-metal layer in the model comprises molybdenum. FIG. 6(b) models the molybdenum-containing composite in the symmetrical half-plane. As is clearly shown, the thermally loaded structure 37 is quite deformed from the stress-free structure

38. In this case, the molybdenum metal layer linearly expands at a rate ( $\alpha_{\text{molybdenum}} = 5.43 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) that is less than both the rates for the ceramic member ( $\alpha_{\text{alumina}} = 8.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) and the copper member ( $\alpha_{\text{copper}} = 16.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) to which it is attached. In fact, stress analysis shows that the von Mises stresses in a metal-ceramic composite printed circuit board substrate containing a molybdenum constraining-metal layer situated as depicted in FIG. 6(a) are, in fact, greater than the von Mises stresses for a metal-ceramic composite printed circuit board substrate that does not contain the molybdenum constraining-metal member.

FIG. 6(c) depicts a magnified view (20x) of the FEM-simulated deformation to the metal-ceramic composite when the constraining-metal layer in the model comprises titanium. Again, FIG. 6(c) models the composite in the symmetrical half-plane. As is clearly shown, structural deformation to a metal-ceramic composite printed circuit board substrate containing a titanium constraining-metal member directly bonded to the ceramic member is generated by thermal loading 39 when compared to the stress-free structure 38. This deformation is greatly reduced when compared to the deformation generated in the thermally loaded metal-ceramic composite that contains a molybdenum constraining-metal member. Titanium has a coefficient-of-thermal-expansion ( $\alpha_{\text{titanium}} = 8.33 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) that is a far better match with alumina ( $\alpha_{\text{alumina}} = 8.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ), and, as a result, reduces von Mises stress in the ceramic by more than 50%.

The improved structure cannot be reduced to practice using a high-temperature process, such as those described by the prior art. As reported by Kashiba *et al.*, titanium and copper form an eutectic at temperatures greater than 880 °C. Therefore, a process that requires a copper member to be mechanically pressed to a titanium member at a temperature of at least 900 °C for a period of at least 20 minutes will cause the members to form their eutectic and liquefy. Under the present invention, a covalent bond is formed between the deposited ceramic member and the metal member(s) at temperatures less than 550 °C. As such, the present invention makes possible the construction of a much wider variety of high electrical or high thermal conductivity metal member bonded to constraining-metal member combinations. It is, therefore, a preferred embodiment of the present invention to deposit a ceramic member on a metallic member substrate, wherein the metallic member substrate comprises at least one high coefficient-of-thermal-expansion metal member consisting of a pure metal, metal alloy, or metal composite of aluminum, copper, silver, or gold, that is bonded, on at least one major surface, to a constraining metal member, wherein the constraining-metal member may comprise a pure metal, metal alloy or metal composite of antimony, chromium, iridium, molybdenum, tantalum, ( $\alpha$ -)tin, titanium, tungsten, or vanadium. The high coefficient-of-thermal-expansion metal member may be characterized as having a high electrical conductivity and/or

high thermal conductivity. The constraining-metal member bonded to the metal member with a high coefficient-of-thermal-expansion may be characterized as having a coefficient-of-thermal-expansion that is less than the coefficient of expansion of the metal member to which it is bonded. It is preferred to have the constraining-metal member bonded to the metal member having a high coefficient-of-thermal-expansion through explosive pressure welding, or other metal-metal bonding techniques known to practitioners skilled in the art of metallurgy, prior to forming a covalent bond with the deposited ceramic member.

The ability to form a covalent bond between the deposited ceramic member and the metallic substrate without a molten bonding agent or adhesive, as is enabled under the present invention, permits even greater improvement to the prior art by introducing stress-reducing micro-mechanical elements to the interface. The present invention allows, as shown in FIG. 7(a) for at least one adhesion-resistant body 40 to be placed on the surface of the metal member substrate 41 onto which the ceramic member will be deposited prior to depositing the ceramic member. The adhesion-resistant body can be blown off the surface of the metal member substrate during the ceramic deposition process, therefore it is a preferred embodiment of this invention to physically secure the at least one adhesion-resistant body on the surface of the metal member substrate without forming a permanent bond between the at least one adhesion-resistant body and the



metal member substrate by coating the adhesion-resistant body with a resin epoxy 42 as shown in FIG. 7(b)) that decomposes at temperatures greater than the substrate deposition temperature to which the metal member substrate is heated during the ceramic deposition process. The ceramic member 43 as shown in FIG. 7(c) is then spray pyrolyzed from a metalorganic solution on to the metal member substrate 41 and the at least one adhesion-resistant body 40 physically attached to or placed on the metal member substrate and processed to form the metal-ceramic composite. After the deposited ceramic member 43 has been formed to a sufficient thickness on the metal member substrate and the at least one adhesion-resistant body, the entire metal-ceramic composite can be heated to a temperature that decomposes the resin epoxy 42 that physically secures the at least one adhesion-resistant body to the metal member substrate, (typically to a temperature in the range between 450 °C to 550 °C), to produce a metal-ceramic composite in which a rigid covalent bond has been formed between the metal member substrate 41 and the deposited ceramic member 43 only at those regions of the metal-ceramic interface that are not occupied by the at least one adhesion resistant body 44 as shown in FIG. 7(d). If the adhesion-resistant body is composed of a material composition and phase that does not liquefy and form a rigid bond through molten action, regions 45 of the metal-ceramic interface that are occupied by the at least one adhesion resistant body will not be

bonded to the adhesion-resistant body, nor to the deposited ceramic layer. The adhesion-resistant body 40 will be allowed to slip relative to displacements or linear expansions of the metal member substrate 41 at the non-bonded regions 45 of the metal-ceramic interface. This embodiment of the present invention cannot be produced using metal-ceramic bonding techniques, such as eutectic bonding or active metal/solder bonding, which form the bond through a liquefied or molten phase that, when pressed, is smeared, and forms a rigid bond when cooled, across the entire bonding surface.

The cross-sectional geometry of each adhesion-resistant body need not be circular as depicted in drawings and may assume any cross-sectional geometry that improves the crack-resistance of the deposited ceramic member, or reduces the stress distribution within the metal-ceramic composite. The cross-sectional geometry for the adhesion-resistant body can be determined for a given application using computer simulation by any practitioner skilled in the art of finite element method analysis. Similarly, the at least one adhesion-resistant body need not be a discrete body, but a series of continuous bodies, such as whiskers, platelets or fibers. For instance, a fiber or wire mesh can be utilized to pattern a adhesion-resistant body grid at the metal-ceramic interface. In certain specific applications specific patterns of adhesion-resistant bodies, which might comprise adhesion-resistant bodies of differing cross-sectional geometry, or a combination of discrete and continuous

adhesion-resistant bodies of varying shapes and sizes, are preferred.

FIGS. 8 (a) and (b) represent top perspectives of some, but by no means all, representative patterns of adhesion-resistant bodies 40 on metal member substrates 41 that may be useful. Such patterns of adhesion-resistant bodies can be fixed on the surface of the metal member substrate using a variety of means, including, but not limited to, screen printing or other printing techniques such as, letterpress, gravure, rotogravure, dot and or jet printing. A particular pattern of adhesion-resistant bodies will, of course, be dependent upon on the thermal and/or mechanical loads of a specific application, and can be determined using computer simulation by any practitioner skilled in the art of finite element method analysis or other computer simulation methods. The use of adhesion-resistant bodies to construct a metal-ceramic composite with improved interfacial properties in any pattern is considered an element of, and as having been instructed by, the present invention.

The adhesion-resistant bodies may be produced from a variety of materials that do not liquefy or form a molten or rigid bond with the metal member to which the adhesion-resistant bodies are contacted in a metal-ceramic composite. Therefore, its is recommended to compose the adhesion-resistant bodies from a material that melts at temperatures greater than the maximum temperatures (450-880 °C) to which the metal-ceramic composite may be exposed. the adhesion-resistant bodies may be

composed of materials that comprise, but are not limited to, metals or metal alloys, a glass phase, a shape memory alloy, graphite, an oxide or non-oxide material, or a crystalline ceramic or single crystal material phase.

As shown in FIGS. 9 (a) and (b) it is another preferred embodiment of this invention to utilize adhesion-resistant bodies composed of a material phase that can be selectively etched or removed from the metal-ceramic composite after processing to produce voids 46 in the deposited ceramic member 43 bonded to the metal member substrate 41 of the metal-ceramic composite where the selectively etchable adhesion-resistant bodies were originally located as shown in FIG. 9(a). This aspect of the invention allows micro-mechanical struts 47 to be produced in the ceramic member that can flex in response to lateral displacements of the bonded metal member caused by linear expansions or contractions of the bonded metal member. FIG. 9(b) depicts the flexure in a thermally loaded composite 39 compared to its stress-free state 38. The flexure provided by the micro-mechanical struts in the ceramic member reduces the shear stresses normally generated in the interior of a bonded ceramic member which typically induce cracking of the bonded ceramic member. The degree of stress reduction in the bonded ceramic member is dependent upon the physical dimensions of the micro-mechanical struts, which may be defined as having a width,  $w$ , a depth,  $d$ , and a spacing,  $s$  as shown in FIG. 9(a). FIG. 10 graphically depicts characteristic curves for the stress

reduction in the ceramic member at distances of 20 microns A , 52 microns B, and 185 microns C versus the depth parameter (d-parameter) of micro-mechanical struts that have a width (w-parameter) of 50 microns, and a spacing (s-parameter) equal to 50 microns. FIG. 11 depicts characteristics curves for the stress reduction in the ceramic member at distances of 20 microns D, 52 microns E, and 185 microns F versus the width parameter (w-parameter) of micro-mechanical struts that have a depth (d-parameter) of 150 microns, and a spacing (s-parameter) equal to 50 microns.

Hygroscopic glass materials are preferred for use as the selectively etchable adhesion-resistant body materials used to produce patterns of voids and micro-mechanical struts in the bonded ceramic member. Hygroscopic glass materials can be dissolved in water without risking erosion of the composites metal and ceramic members by simply immersing the composite into an aqueous ultrasonic bath medium. Glass materials can be easily shaped into microscopic geometries and patterns using methods well known to practitioners skilled in the art of producing optical fiber, fiber-optic bundles, and micro-optical components. It is a preferred embodiment of this invention to utilize phosphate-based and or borate-based hygroscopic oxide glasses as the selectively etchable adhesion-resistant bodies.

— EMI Resistant Panels

A particular aspect of the metal-ceramic composites of the present invention relates to the use of the metal-ceramic composites as a device to absorb or shield electromagnetic radiation. The device comprises a lossy ferrite ceramic bonded to a metallic substrate. The lossy ferrite ceramic serves as a microwave field attenuator and absorbs microwave signals directed towards, converting the absorbed microwave signal into heat. The metallic substrate serves to dissipate the generated heat. Ferrite absorption of microwave frequencies relate to magnetic dipoles within the ferrite that become resonant with the applied microwave field. The power of the electromagnetic field is absorbed as it excites a resonant response in the ferrite ceramic. Power absorption by a ferrite ceramic can be made to be particularly acute to a certain frequency using an applied magnetic field.

Ferrite ceramics, like ferrous metals, are magnetic materials, and, as a result will retain a remnant field when magnetized. Many applications for the microwave field attenuating devices requires the devices to be situated in close proximity to electronic circuitry, with which an applied or remnant magnetic field could interfere. Ferrite ceramics have much lower magnetic permeabilities than ferrous metals, and, as such are preferred in applications that might be sensitive to a nearby magnetized member. Therefore, it is a preferred embodiment of this invention to engineer the

material properties of the ferrite ceramic to have strong microwave absorption (high loss) at high (microwave) frequencies with minimal applied or remnant magnetic fields.

Ferrites exhibit high loss under low (or zero) applied magnetic fields through a mechanism known as low-field loss as shown in FIG. 12. Loss mechanisms driving low-field losses occur over a frequency range  $\omega_{\min}$  and  $\omega_{\max}$ , defined as:

$$\omega_{\min} = \gamma H_a, \quad (2a)$$

and,

$$\omega_{\max} = \gamma (H_a + M_0/\mu) \quad (2b)$$

where  $\gamma$  is the gyromagnetic factor,  $H_a$  is crystalline anisotropy field of the ceramic,  $M_0$  is the saturation magnetization of the ceramic, and  $\mu$  is the magnetic permeability of the ceramic. If the metal-ferrite ceramic composite device is designed to operate at a characteristic frequency,  $\omega_{op}$ , the intrinsic properties of the ferrite ceramic member in the composite should be such that the characteristic frequency,  $\omega_{op}$ , should be within the range of low-field losses defined by  $\omega_{\min}$  and  $\omega_{\max}$ . Therefore, for the metal-ferrite ceramic composite device to function effectively at  $\omega_{op}$ , the ferrite ceramic member must have a crystalline anisotropy field,  $H_a$ , a saturation magnetization,  $M_0$ , and a magnetic permeability,  $\mu$ , such that

$$H_a \leq \omega_{op}/\gamma \leq H_a + M_0/\mu. \quad (3)$$

It is a preferred embodiment of the invention that the thickness of the ferrite ceramic member be less than 2.0 mm. Signal attenuation,  $a_{loss}$ , in

a ferrite ceramic can be evaluated from the magnetic permeability,  $\mu$ , electrical permittivity,  $\epsilon$ , and the loss tangent,  $\tan\delta$ , (the ratio of the imaginary component to the real component of the magnetic permeability), calculated as,

$$\alpha_{\text{loss}} = 1/2 \omega_{\text{op}} (\mu\epsilon) [(1 + \tan^2\delta)^{1/2} - 1]^{1/2}. \quad (4)$$

As such, in order to be at least partially effective in absorbing electromagnetic radiation, the ferrite ceramic member should have a loss tangent, such that  $\tan\delta > 3$ , and a real permeability  $\mu'$  and electrical permittivity  $\epsilon$ , such that,  $\mu' \times \omega_{\text{op}}^2 > 10,000/\epsilon$ . It is preferred that the metal member in the metal-ferrite ceramic have a thickness in the range between 0.01 mm to 5.00 mm, and that the thickness of the ferrite ceramic be in the range between 0.1 mm to 5.0 mm.

High frequency (microwave) signal loss in ferrite ceramics increases when the grain sizes in the ceramic are large and densely packed. The present invention is particularly useful in producing large densely packed ceramic grains bonded to a thermally conductive metal substrate. Certain metal oxide additives also promote the growth of large grains in ferrite ceramics. One can incorporate additives of manganese, vanadium, niobium, lead, copper, antimony and/or titanium oxides into the primary (ferrite) ceramic phase of the metal-



ferrite ceramic composite device. The primary phase plus the additive oxides forming a solid solution under pyrolysis heating and/or subsequent processing conditions.

#### Printed Circuit Boards

Another particular aspect of the metal-ceramic composites of this invention relates to the use of the metal-ceramic composites as a metal-ceramic composite substrate for printed circuit boards. As discussed above, metal-ceramic composite substrates for printed circuit boards comprise a high conductivity metal sheet member, commonly a copper sheet on which semiconductor integrated circuits are eventually mounted. The metal sheet member is bonded on a major surface to an insulating ceramic member with a low-dielectric constant, typically alumina, which, in turn, is bonded on its opposing major to another high conductivity metal (copper) sheet. The copper sheet upon which SIC's are eventually mounted is required to satisfy certain tolerances for the metal-ceramic composite substrate to operate reliably as a printed circuit board, and may contain a constraining-metal member to reduce its effective coefficient-of-thermal-expansion.

Tolerances relating to the surface roughness of the metal member on which SIC's are mounted require the metal member to have at least a median surface roughness of 3 microns and a maximum surface of 18 microns, although a median surface roughness of 1 micron and a maximum surface roughness of 8 microns are

preferred. It is also preferable to chemically polish the metal member in a mixture of sulfuric acid and hydrogen peroxide for a period of 1 to 5 minutes to attain a surface finish within these tolerances. Tolerances relating to the Vickers hardness of the metal member on which SIC's are mounted require the metal member to have a Vickers hardness that is at least in the range of 40-100 Kg/mm<sup>2</sup>, although a Vickers hardness in the range of 60-80 Kg/mm<sup>2</sup> is preferred.

Metal-ceramic composites formed by spray pyrolyzing the ceramic member on the metal member from a metalorganic precursor solution permits the production of metal-ceramic-metal composite sheet structures by pressing together two composites ceramic face to ceramic face, wherein the composites comprise a ceramic member deposited on a metal member substrate. The pressed metal-ceramic-metal composite is then thermomechanically calcined to form a uniformly rigidly bonded structure. This application of the present invention is suitable for composites structures in which the ceramic members can be sintered at temperatures less than the melting point of the metal member substrates. This is not possible with copper-alumina-copper structures, wherein the alumina member needs to be sintered at a temperature of at least 1828 °C, which is well above the melting point of copper at 1083°C.

Also under the present invention, high conductivity metal-alumina-high conductivity metal, such as copper-alumina-copper structures, with improved crack-resistance and interfacial properties are produced by

depositing an alumina-based ceramic on the high conductivity metal member. As shown in FIGS. 13 and 14(a) and (b) it is another preferred embodiment of the present invention for the high conductivity metal member substrate 53 upon which an alumina ceramic member 54 is deposited to contain a constraining-metal member 55, and for adhesion-resistant bodies 56 to be implanted at the interface between the metal member substrate and the deposited ceramic member. A similarly made metal-alumina ceramic composite, which may or may not contain the constraining-metal member 55 or the adhesion-resistant bodies 56, is produced to bond with the other metal-alumina ceramic composite. Low temperature ( $<880^{\circ}\text{C}$ ) bonding is achieved by introducing a layer of low-melting temperature oxide or oxyfluoride phase materials 57 that form a molten liquid phase at temperatures below  $880^{\circ}\text{C}$  on the bonding surfaces 58 of at least one the metal-alumina ceramic composites. The low-temperature oxide or oxyfluoride phases may be introduced to the bonding surface as metalorganic precursors of the spray pyrolyzed solution, as secondary phase material particles dispersed in the metalorganic solution, as secondary phase material particles not dispersed in the metalorganic solution but still applied to the bonding surfaces 58, are as an active metal film or powders that are oxidized. In printed circuit board applications it is desirable for the bonded alumina ceramic member to have a low dielectric constant, it is, therefore, preferable to use light atomic weight

metal oxides. It is a preferred embodiment of this invention to utilize an phospho-alumino-borate glass phase as the low-temperature oxide bonding layer. Borate glass melts at temperatures as low as 450 °C, but is sensitive to chemical attack by water. Phosphoric anhydride typically melts in the range of 580-585 °C. Incorporating alumina into phosphate and borate oxide glasses increases chemical resistance and intrinsic strength. Aluminophosphate glass phases typically melt at temperatures ranging from 660-1575 °C. Thus, it is preferable to add borate glass phases to the low-temperature bonding materials when the metallic substrate member in the bonded metal-ceramic composite contains an aluminum member which melts at 660 °C. Additions of alkali oxides or alkali fluorides are useful in depressing the melting temperature of the low-temperature oxide bonding agent, but will also decrease its resistance to chemical attack by water.

It is a further preferred embodiment of this invention for the low melting temperature oxide bonding layer to have a thickness in the range of 1 micron to 150 microns. The two metal-alumina ceramic composites, with at least one of the metal-alumina ceramic composites containing a low-temperature oxide bonding agent on its bonding surface, are then heated to at least a temperature above which the low-temperature oxide bonding agents forms a molten phase. The two metal-alumina ceramic composites are then joined at their bonding surfaces and pressed together at a pressure

between 0.5 and 25 MPa. When cooled, a rigid oxide bond is formed between the two metal-alumina ceramic composites at the bonding surfaces to form the finished conducting metal-alumina ceramic-conducting metal composite. It is generally preferred that the two different metal members in a composite substrate for printed circuit board applications be made to different thickness and mechanical specifications. These differences need to be considered prior to forming the final bonded composite. It is, therefore, a preferred embodiment of this invention to form the composite substrate using one metal-alumina ceramic composite that contains a conducting metal member bonded to a constraining metal member, wherein the thickness of the constraining-metal member is in the range between 0.015 mm to 1.67 mm, and the total (combined) thickness of the conducting metal member(s) is in the range between 0.30 mm to 5.00 mm; and, another metal-alumina ceramic composite that contains a conducting member in the range of 0.01 mm to 0.3 mm. The alumina-ceramic members on each of the two metal-ceramic composites may vary such that the combined thickness of alumina ceramic in the bonded metal-ceramic-metal composite is in the range between 0.3 to 1.0 mm. It is, thus, preferred that the thickness of the ceramic member in the metal-ceramic composites be in the range of 0.15 to 0.85 mm.

Yet another particular subject of the present invention relates to the incorporation of a ferrite ceramic member into a metal-ceramic

composite substrate for printed circuit board applications. In many applications, semiconductor integrated circuits mounted on a printed circuit board substrate may actually become radiators of harmful electromagnetic radiation, or be exceptionally sensitive to such emissions. Thus, as shown in FIGS. 16(a), (b) and 17, it is desirable to have an element in close proximity to the SIC that would absorb the electromagnetic radiation. Under the present invention a lossy ferrite ceramic member 59 can be bonded to a major surface of a high conductivity metal sheet, which is then used, on its opposing major surface, as the metal member substrate for a deposited alumina ceramic member. The ferrite ceramic-metal-alumina ceramic member is then bonded into a metal-ceramic composite substrate suitable for printed circuit board applications using the art described above.

A further particular subject of the present invention relates to the production of a metal-porous ceramic composite, wherein the porous ceramic member has ultrafine subdivision. In certain applications it is desirable for the metal-ceramic composite to function simultaneously as a heat shield and as a sound absorber. A porous ceramic member can function both as a thermally insulating member and as a sound absorber. Porous ceramics are also preferred forms of ceramic in the application of metal-ceramic composites as electrochemical electrodes. Large organic molecules, such as carboxylic acids, generate considerable water and carbon dioxide/carbon monoxide during

thermal decomposition. The formation of a porous ceramic on a metal substrate is readily realized by spray pyrolyzing carboxylic acid salt precursors to the ceramic as the metalorganic solution. Under this aspect of the present invention, mechanical swaging steps are omitted. It may also be preferable to introduce other foaming agents to the metalorganic precursor solution, such as polyurethanes, polyvinylchlorides, polyethylenes, pentanes, hexanes, or polypropylenes, that further increase the foaming actions during the deposition process.

Although the invention has been described with reference to particular embodiments, it will be understood that this invention is also capable of further and other embodiments within the spirit and scope of the appended claims.

What is claimed is:

## CLAIMS

1. A printed circuit board comprising a metal member directly bonded to a ceramic member via a covalent bond, the bond being formed at less than 500° C, the metal member and the ceramic member providing heat dissipation for at least one SIC mounted on the metal member and the metal member providing electrical conductivity for the at least one SIC mounted on the metal member, the metal member having a 3 microns or less surface roughness and a hardness of 40 to 100 Kg/mm<sup>2</sup>,  
the ceramic member comprising a ceramic medium whose precursors have been mixed at the molecular level.
2. The printed circuit board of claim 1 wherein the ceramic comprises an oxide.
3. The printed circuit board of claim 2 wherein the oxide is Al<sub>2</sub>O<sub>3</sub>.
4. The printed circuit board of claim 1 wherein the ceramic member is composed of the ceramic medium containing particles of a secondary phase material dispersed therein to arrest crack propagation.
5. The printed circuit board of claim 4 wherein the secondary phase material has a Young's modulus different than Young's modulus of the ceramic medium.



6. The printed circuit board of claim 1 as made by dispersion of at least one metal organic precursor on a surface of the metal member and pyrolysis of the same at 500° C or less.
7. The printed circuit board of claim 6 as so made and with the further step of thermomechanical densification of the ceramic.
8. The printed circuit board of claim 6 wherein the dispersion is accomplished by spray application.
9. A laminated printed circuit board comprising two of the printed circuit boards of claim 1 bonded ceramic face-to-ceramic face to establish a complete metal-ceramic-metal printed circuit board.
10. A laminated printed circuit board as in claim 9 with an intermediate bonding agent between the bonded faces.
11. The printed circuit board as in claim 1 with cavities in the ceramic member adjacent the metal member.
12. The printed circuit board as in claim 11 wherein said cavities form micromechanical struts in said ceramic layer that can flex in response to lateral displacement of said bonded metal layer caused by linear expansions or contractions of said bonded metal layer.

13. The printed circuit board as in claim 11 with said cavities in the ceramic member formed by including adhesion resistant pieces at preselected locations on a metal surface of the metal member, depositing at least one metal organic precursor at other than said preselected locations on the metal surface and utilizing pyrolysis to form the metal-ceramic covalent bond, except where ceramic adhesion is blocked by the adhesion resistant pieces, and

dissipating the pieces to leave said cavities.

14. The printed circuit board as in claim 13 wherein the adhesion resistant pieces comprise hygroscopic glass.

15. The printed circuit board as in claim 1 with holes (perforations) in the metal member to reduce effective differences between Young's modulus and/or coefficient of thermal expansion of the metal member and such property or properties of the ceramic member.

16. The printed circuit board as in claim 1 wherein the ceramic member is porous.

17. The printed circuit board as in claim 16 further comprising adhesion-resistant pieces on the metal member and being exposed to the ceramic member.

18. The printed circuit board as in claim 17 with means for attaching the adhesion-resistant pieces to the metal member.

19. The printed circuit board as in claim 16 wherein the metal member comprises a high electrical and/or thermal conductivity material selected from the group consisting of:

- (a) elemental metals,
- (b) metal alloys, and
- (c) metal composites of aluminum, copper, gold, or silver, bonded to a constraining-metal member that is 1/20th to 1/3rd the thickness of the high electrical and/or thermal conductivity metal member, wherein the constraining-metal member comprises a metal, metal alloy, or metal composite, of antimony, chromium, iridium, molybdenum, tantalum, tin, titanium, tungsten, or vanadium.

20. The printed circuit board as in claim 1 wherein the metal member comprises a high electrical and/or thermal conductivity material selected from the group consisting of:

- (a) elemental metals,
- (b) metal alloys, and
- (c) metal composites of aluminum, copper, gold, or silver, bonded to a constraining-metal member that is 1/20th to 1/3rd the thickness of the high electrical and/or thermal conductivity metal layer, wherein the constraining-metal member comprises a metal, metal alloy, or metal composite, of antimony, chromium, iridium, molybdenum, tantalum, tin, titanium, tungsten, or vanadium.--

21. The printed circuit board as in claim 1 wherein said ceramic layer provides for EMI shielding.
22. A printed circuit board comprising a metal member bonded directly to a ceramic member via a covalent bond, the bond being formed at less than 500° C, the metal layer and the ceramic layer providing heat dissipation for at least one SIC mounted on the metal member and the metal member providing electrical conductivity for the at least one SIC mounted on the metal member, and  
the ceramic layer being made of a ceramic medium whose precursors have been mixed at the molecular level.
23. An EMI resistant panel comprising a metal layer bonded to a ceramic layer via a covalent bond, the ceramic layer being a lossy ferrite with densely packed ceramic grains of a primary ceramic phase.
24. An EMI resistant panel as in claim 23 comprising secondary ceramic phase additives in the primary ferrite ceramic.
25. An electromagnetic radiating source in combination with the panel of claim 23, the panel being located between the source and a zone to be protected.
26. A personal electronic device comprising the combination of claim 25 as a portion thereof.

27. A ceramic-metal composite as made by

(a) dispersion of a metal organic precursor of the ceramic on a metal layer,

(b) pyrolysis of the precursor at 500° C or less to form the ceramic with a covalent bond to the metal and an absence of intermetallic entectic or ceramic compositional segregation at the metal-ceramic interface, and

(c) densification of the ceramic.

28. An EMI resistant device as in claim 27 with cavities at the ceramic-metal interface.

29. An EMI resistant device as in claim 23 with cavities at the ceramic-metal interface as formed by including adhesion resistant pieces at a metal surface, depositing an organic metal precursor at such surface and pyrolysis to form the metal-ceramic covalent bond at their interface, except where adhesion is blocked by the adhesion resistant pieces, and

dissipating the pieces to leave cavities.

30. The device of claim 29 wherein the adhesion resistant pieces comprise hygroscopic glass.

31. A metal ceramic composite as in claim 27 with holes (perforations) in the metal layer to reduce the effective differences between its Young's modulus and/or coefficient thermal

expansion and such property or properties of the ceramic layer.

32. A metal-ceramic composite, comprising adjacent metal and ceramic primary phase portions, the ceramic being a porous ceramic,

wherein the metal phase portion in the metal-ceramic composite is rigidly attached through a covalent bond to a porous ceramic secondary phase portion with ultrafine subdivision,

the bond being as made by spray pyrolyzing the ceramic from a metalorganic precursor solution to form a covalent bond at the metal ceramic interface.

33. A metal-ceramic composite as in claim 32 wherein the porous ceramic primary phase contains secondary phase material particles dispersed throughout a substantial portion of its volume,

the secondary phase material particles comprising material selected from the group consisting of metals, metal alloys, glass, shape memory alloys, graphite, oxides, non-oxide inert compounds, crystalline ceramics, a single crystalline phase, and combinations of these materials phases.

34. A metal-ceramic composite, comprising adjacent metal and ceramic primary phase portions, the ceramic being a dense ceramic,

wherein the metal phase portion in the metal-ceramic composite is rigidly attached through a covalent bond to a dense

ceramic phase portion with ultrafine subdivision, the bond being as made by spray pyrolyzing the oxide ceramic from a metalorganic precursor solution to form a covalent bond at the metal ceramic interface, and the densifying and crystallizing the spray pyrolyzed ceramic through a repetitive sequence of reaction and mechanical deformation processing steps.

35. A metal-ceramic composite as in claim 34, wherein the dense ceramic primary phase contains secondary phase material particles dispersed substantially throughout a substantial portion of its volume,

the secondary phase material particles comprising material selected from the group consisting of metals, metal alloys, glass, shape memory alloys, graphite, oxide, non-oxide materials, crystalline ceramics, a single crystalline phase, and combinations of these material phases.

36. A metal-ceramic composite as in claim 35, wherein the secondary phase material particles dispersed in the oxide ceramic primary phase portion bonded to the metal phase portion have a size defined by a major axis of such particles with a length ranging between 0.05 and 500 microns.

37. A metal-ceramic composite as in claim 36, wherein the secondary phase material particles dispersed in the oxide ceramic primary phase part bonded to the metal member have a size

defined by a major axis with a length ranging between 0.10 and 50 microns.

38. A metal-ceramic composite as in claim 35 , wherein the oxide ceramic is constructed and arranged with a gradient composition that causes the coefficient-of-thermal-expansion of the oxide ceramic to be greater at distances further away from the surface(s) at which the oxide ceramic member is bonded to the metal member, and lower at the surface(s) at which the oxide ceramic member is bonded to the metal member.

39. A metal-ceramic composite as in claims 35 where the primary ceramic is an oxide.

40. A metal-ceramic composite as in claim 39 wherein the oxide ceramic is  $\text{Al}_2\text{O}_3$ .

41. A metal-ceramic composite as in claim 32 and further comprising adhesion-resistant means between the metal and ceramic primary phase portions.

42. A metal-ceramic composite as in claim 41 with means for bonding the adhesion-resistant means to the metal member.

43. A metal-ceramic composite as in claim 32 wherein the metal comprises a high electrical and/or thermal conductivity material selected from the group consisting of:

- (a) elemental metals,
- (b) metal alloys, and



(c) metal composites of aluminum, copper, gold, or silver, bonded to a constraining-metal member that is 1/20th to 1/3rd the thickness of the high conductivity metal member, wherein the constraining-metal member comprises a metal, metal alloy, or metal composite, of antimony, chromium, iridium, molybdenum, tantalum, tin, titanium, tungsten, or vanadium.

44. A metal-ceramic composite as in claim 32 as made by temporarily bonding an adhesion resistant material to a metal substrate in selected surface regions, spray pyrolyzing ceramic in such regions and removing the adhesion resistant material to form a porous structure.

45. A metal-ceramic composite as in claim 32 as applied to two ceramic containing pieces, at least one of which is a metal-ceramic composite as recited above, the two pieces bonded at respective ceramic surfaces by an intermediate low-melting temperature oxide phase.

46. A bonded structure as recited in claim 45 wherein the low-melting temperature oxide phase used to bond two pieces together ceramic-face to ceramic-face is a phospho-alumino-borate glass phase.

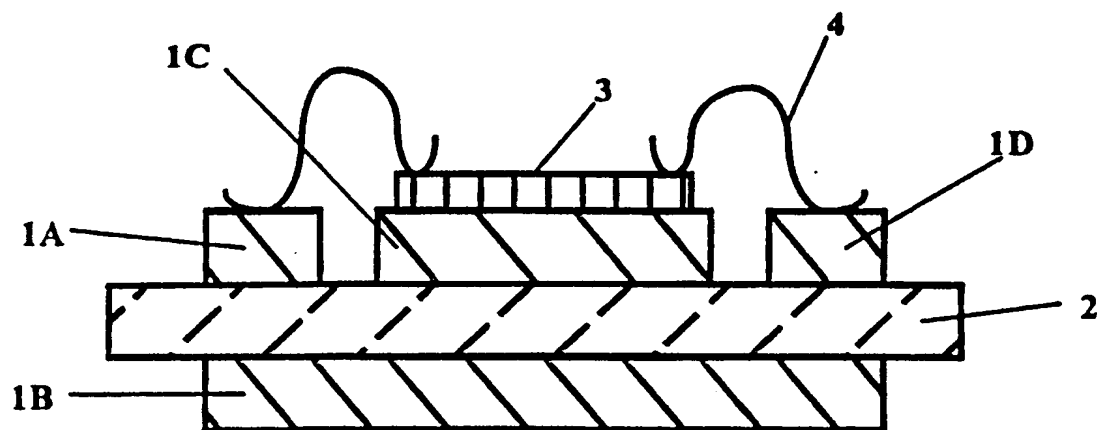
47. A bonded structure as recited in claim 46, wherein two such metal-ceramic composites, the ceramic being alumina, are bonded together to

form a metal-ceramic composite substrate suitable for printed circuit board usage.

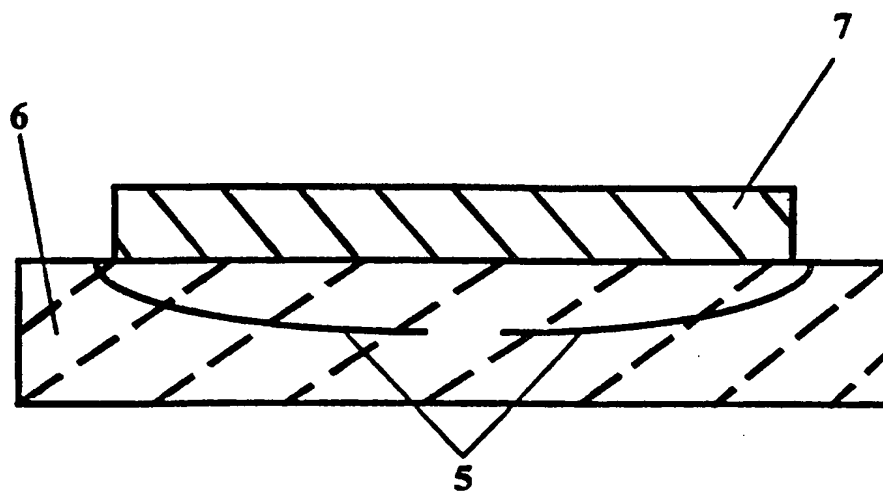
48. A printed circuit board constructed as in claim 47 with a metal portion on which SIC's can be mounted, with a total (combined) thickness of 0.3 mm to 5.00 mm bonded to a constraining metal member that is 0.015 mm to 1.67 mm thick; an alumina ceramic member having thickness in the range between 0.3 mm to 1.00 mm; and a conducting metal member that is 0.01 mm to 0.3 mm thick.

49. A bonded set of metal-ceramic composites, as in claim 32, with a common metal substrate for alumina and ferrite ceramics on two opposed faces of the metal.

50. A bonded set of metal-ceramics-composites as in claim 49 with the alumina face of said alumina-metal-ferrite ceramic bonded set bonded to the alumina ceramic face of another metal-alumina ceramic composite to produce a metal-alumina ceramic-metal-ferrite ceramic composite substrate suitable for printed circuit board applications.



**FIG. 1**  
PRIOR ART



**FIG. 2**

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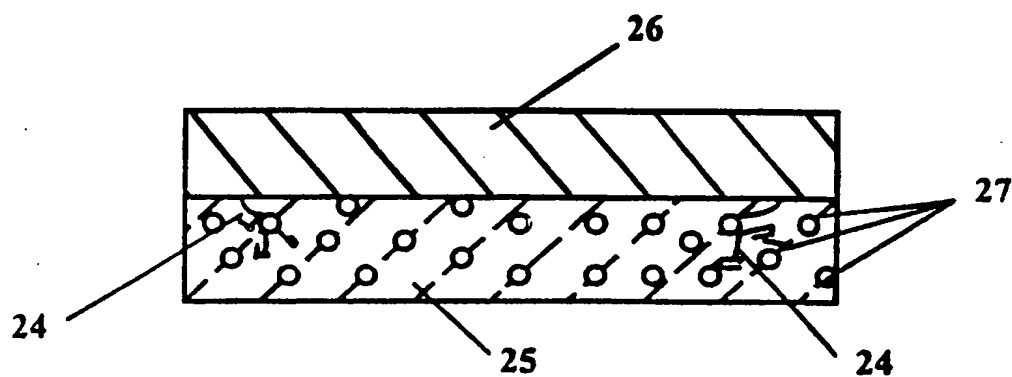


FIG. 3

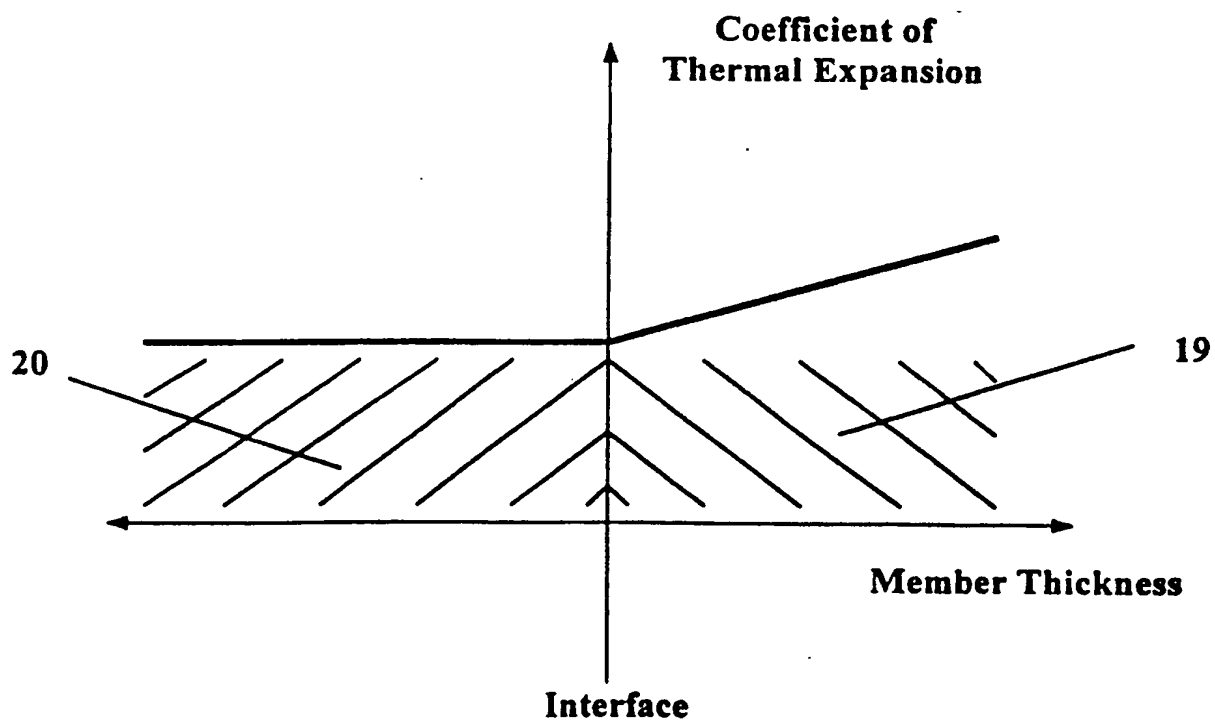


FIG. 4

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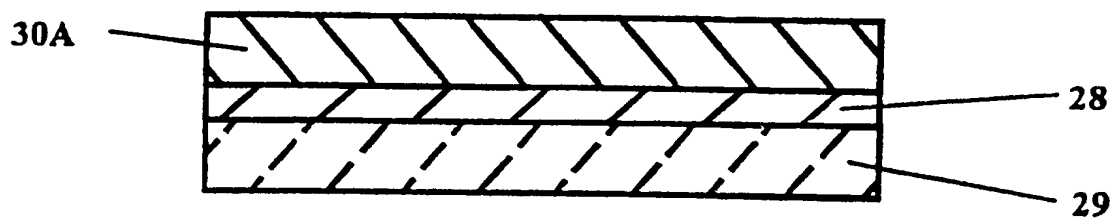


FIG. 5a

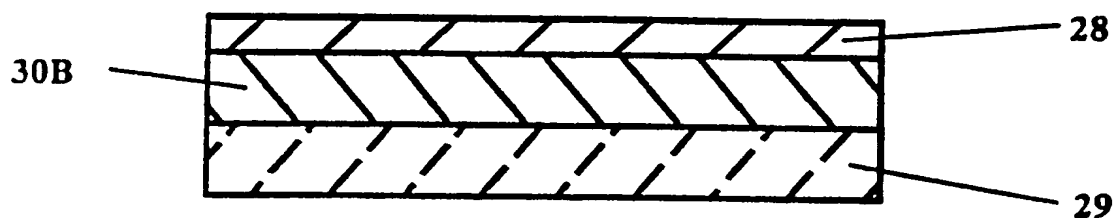


FIG. 5b

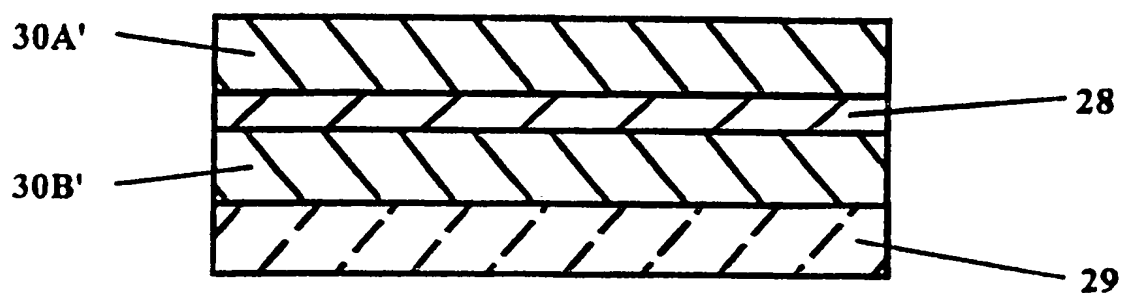


FIG. 5c

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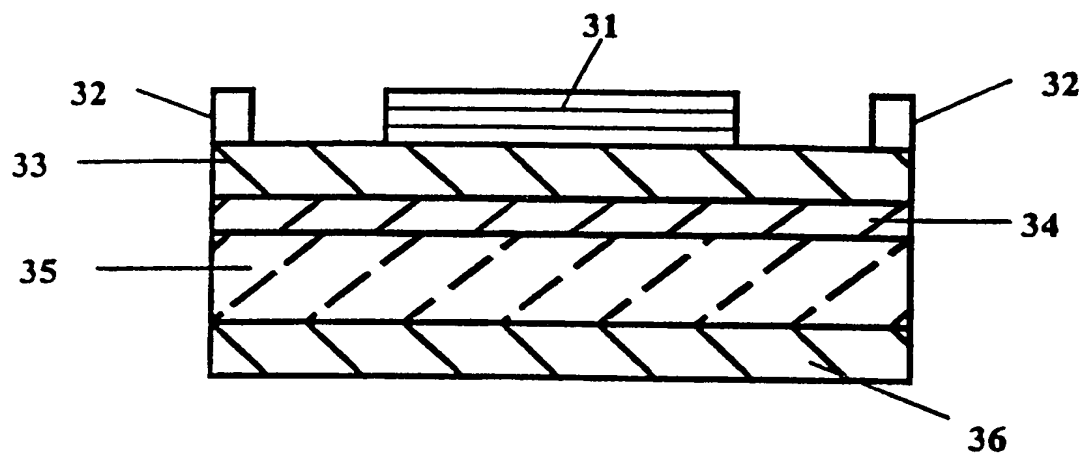


FIG. 6a

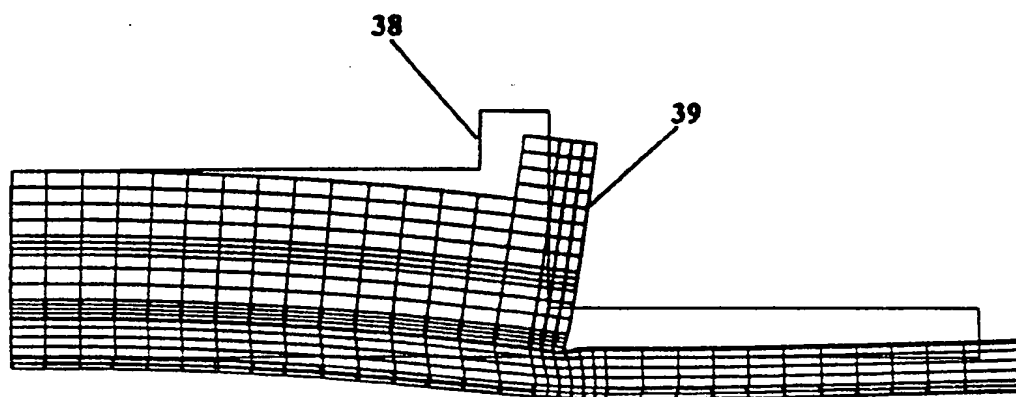


FIG. 6b

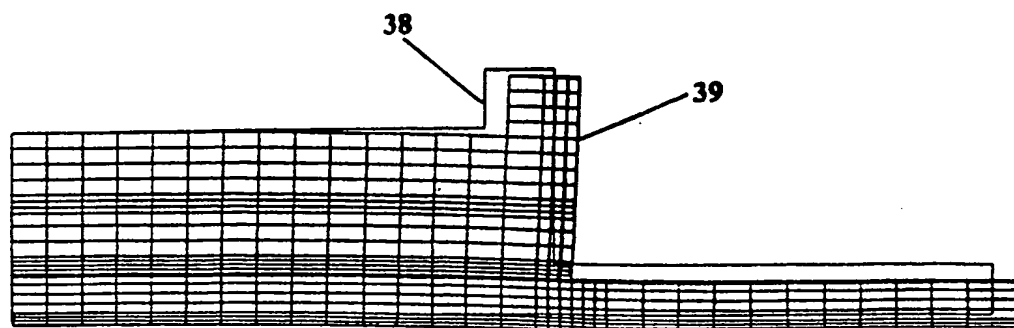


FIG. 6c

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FIG. 7 a

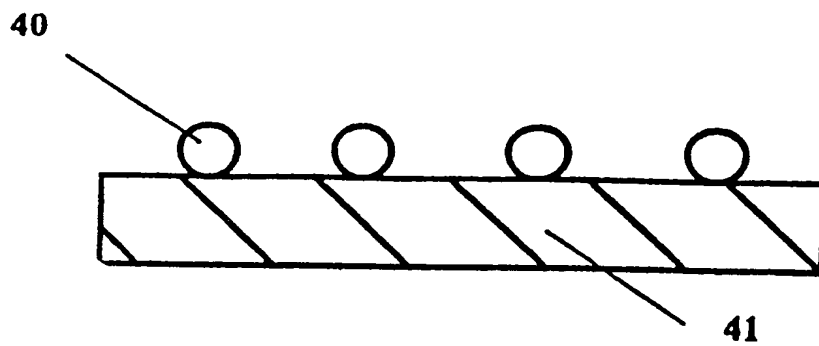


FIG. 7 b

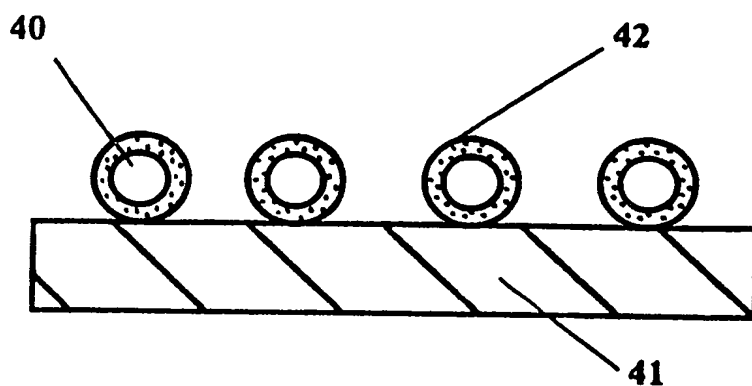


FIG. 7 c

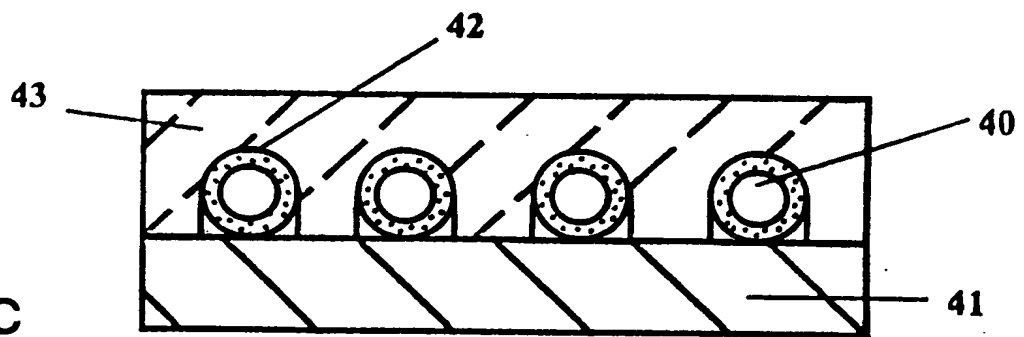
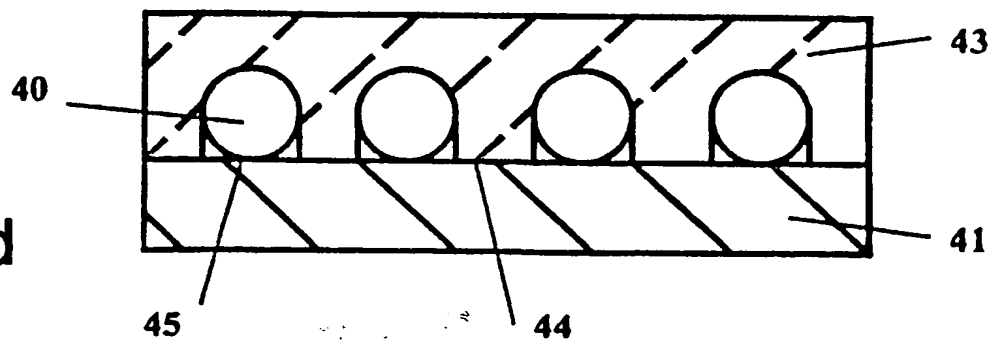


FIG. 7 d



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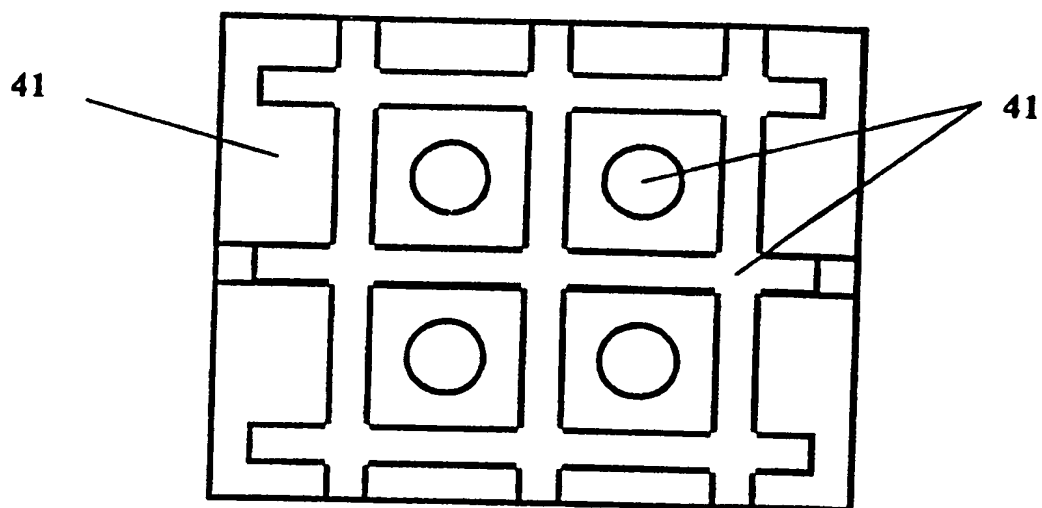


FIG. 8a

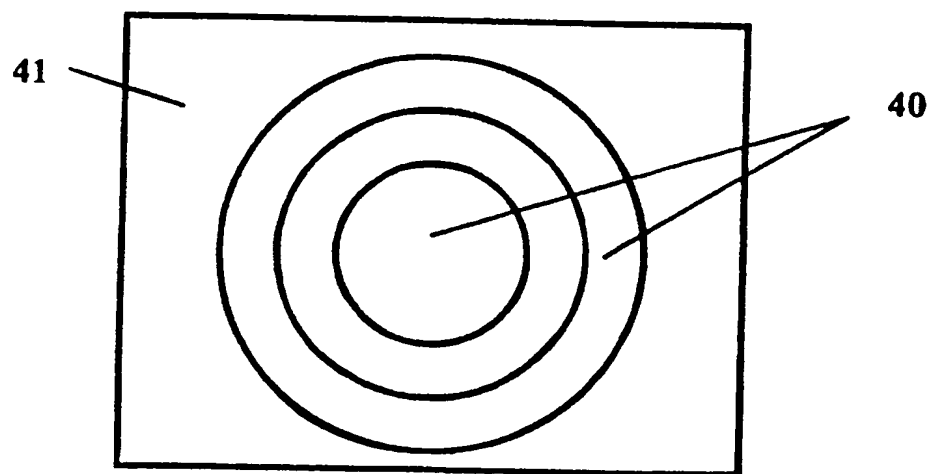


FIG. 8b

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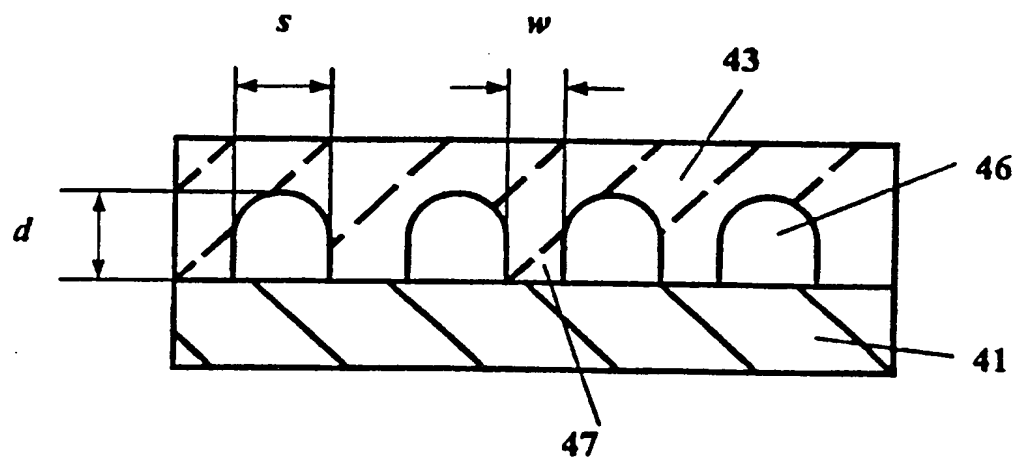


FIG. 9a

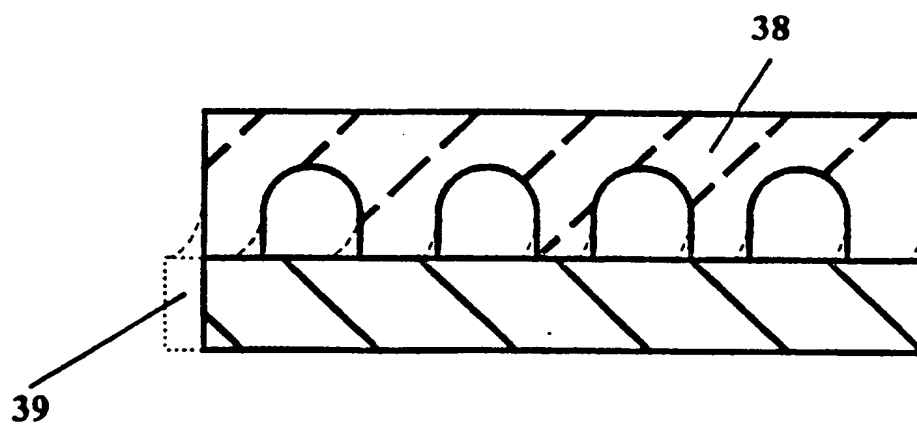


FIG. 9b

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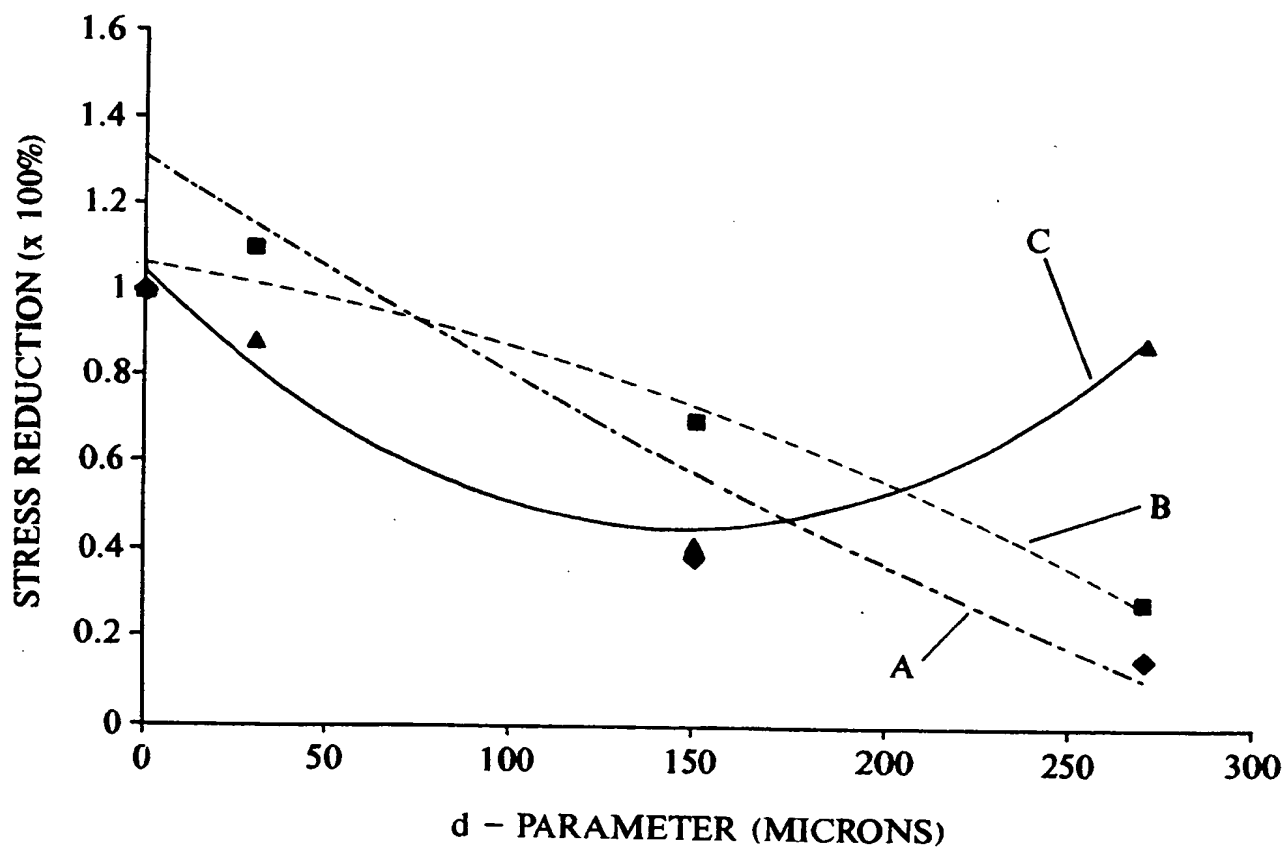


FIG. 10

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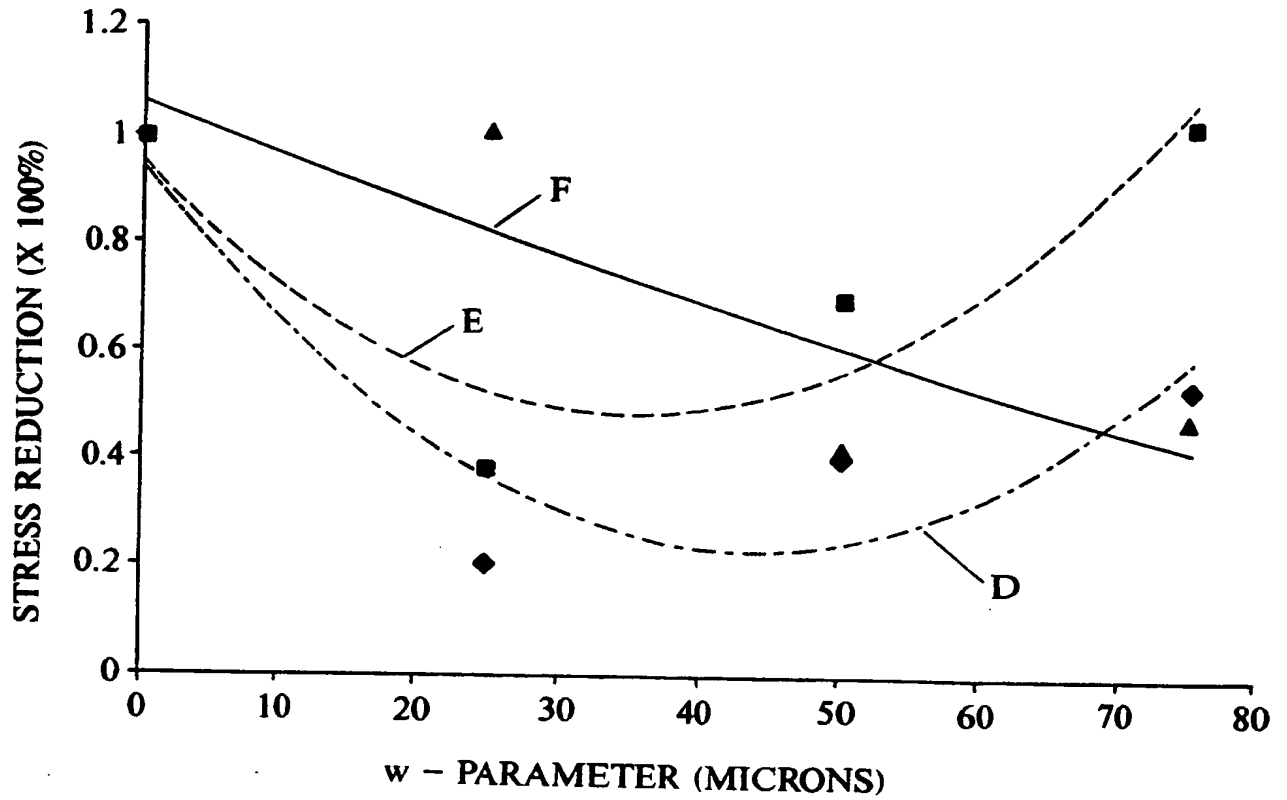


FIG. 11

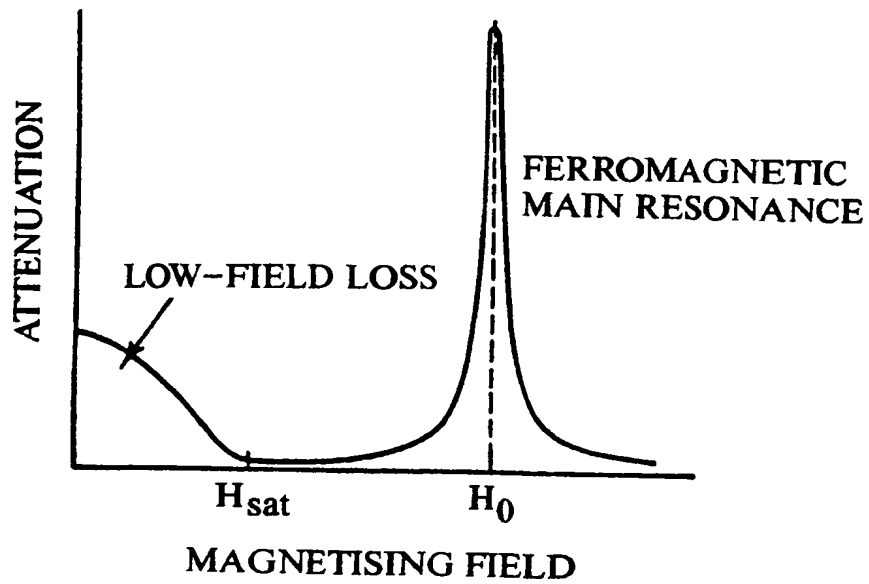


FIG. 12

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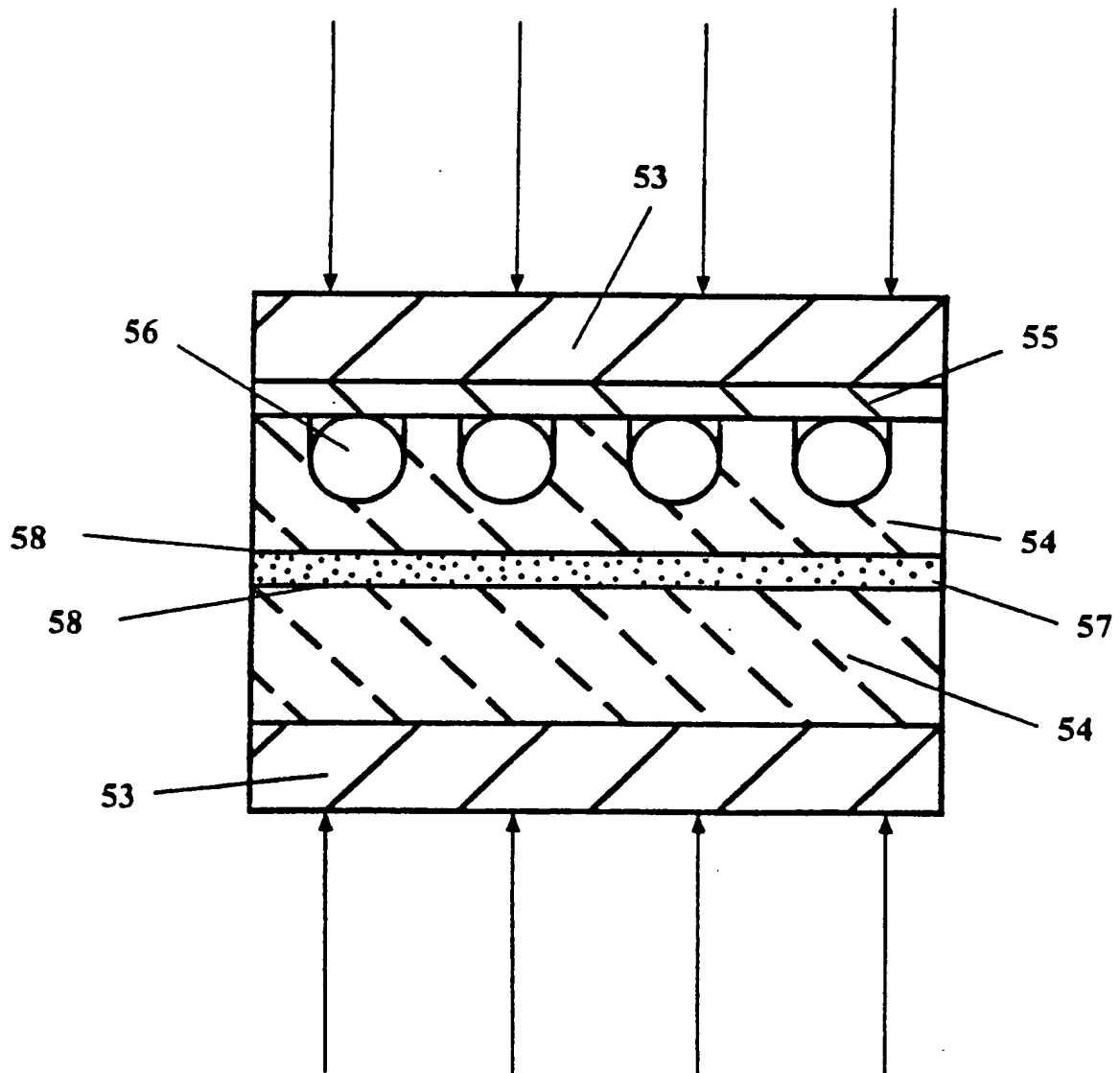
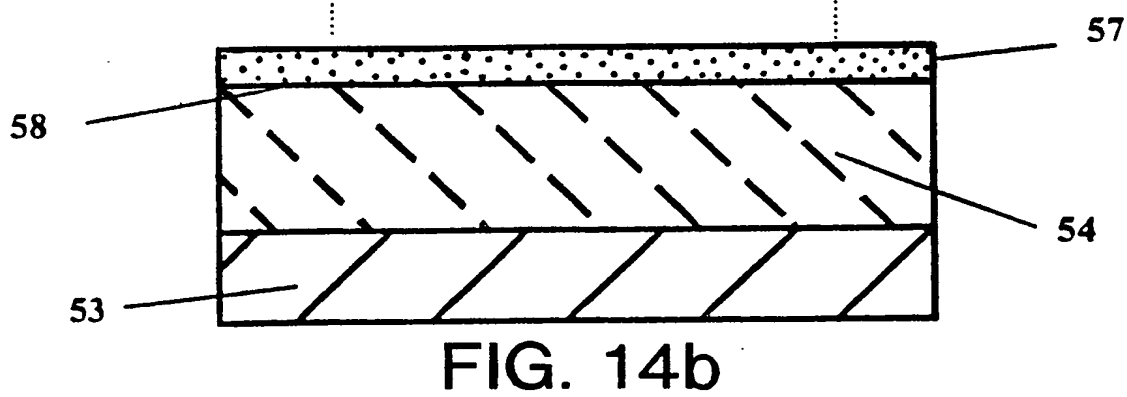
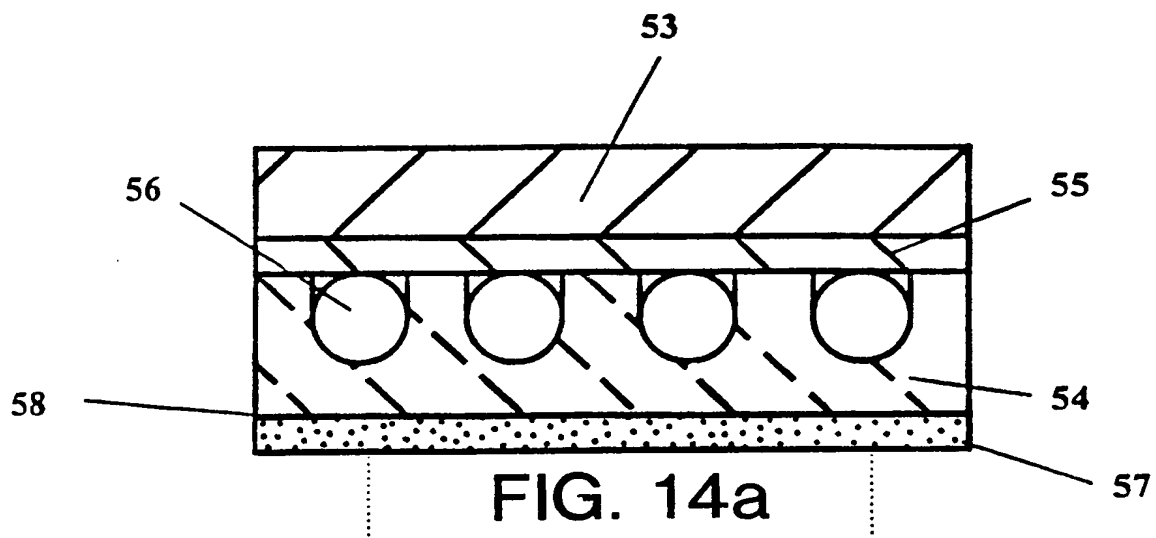


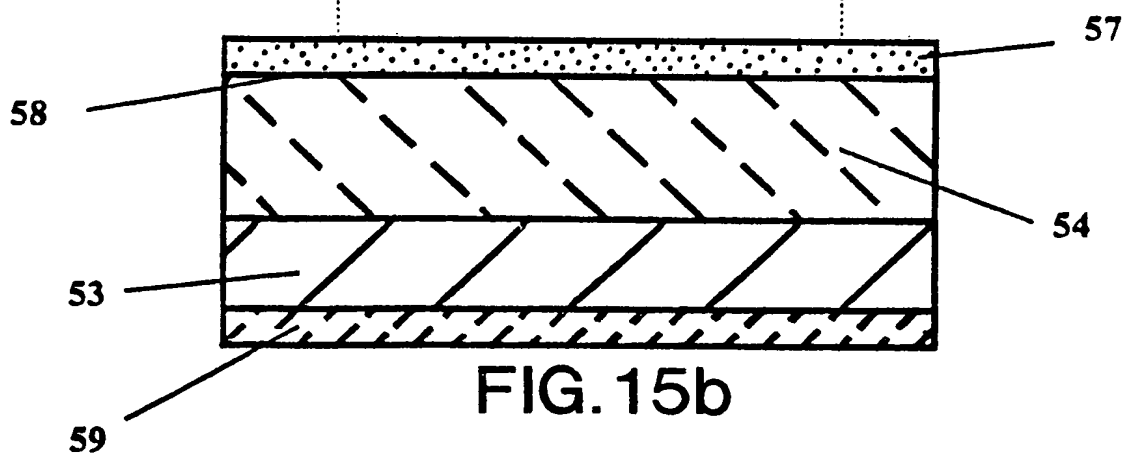
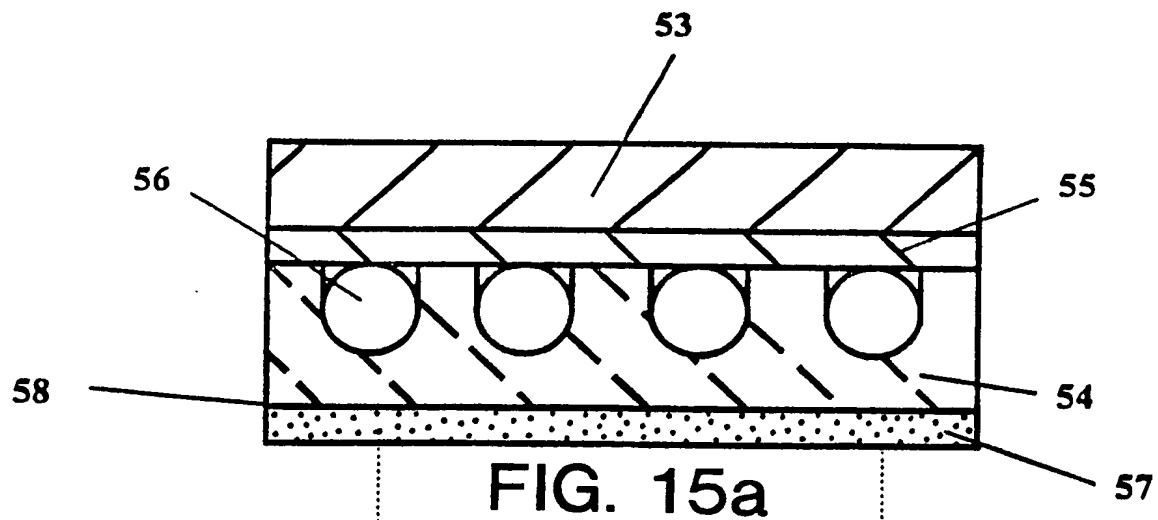
FIG. 13

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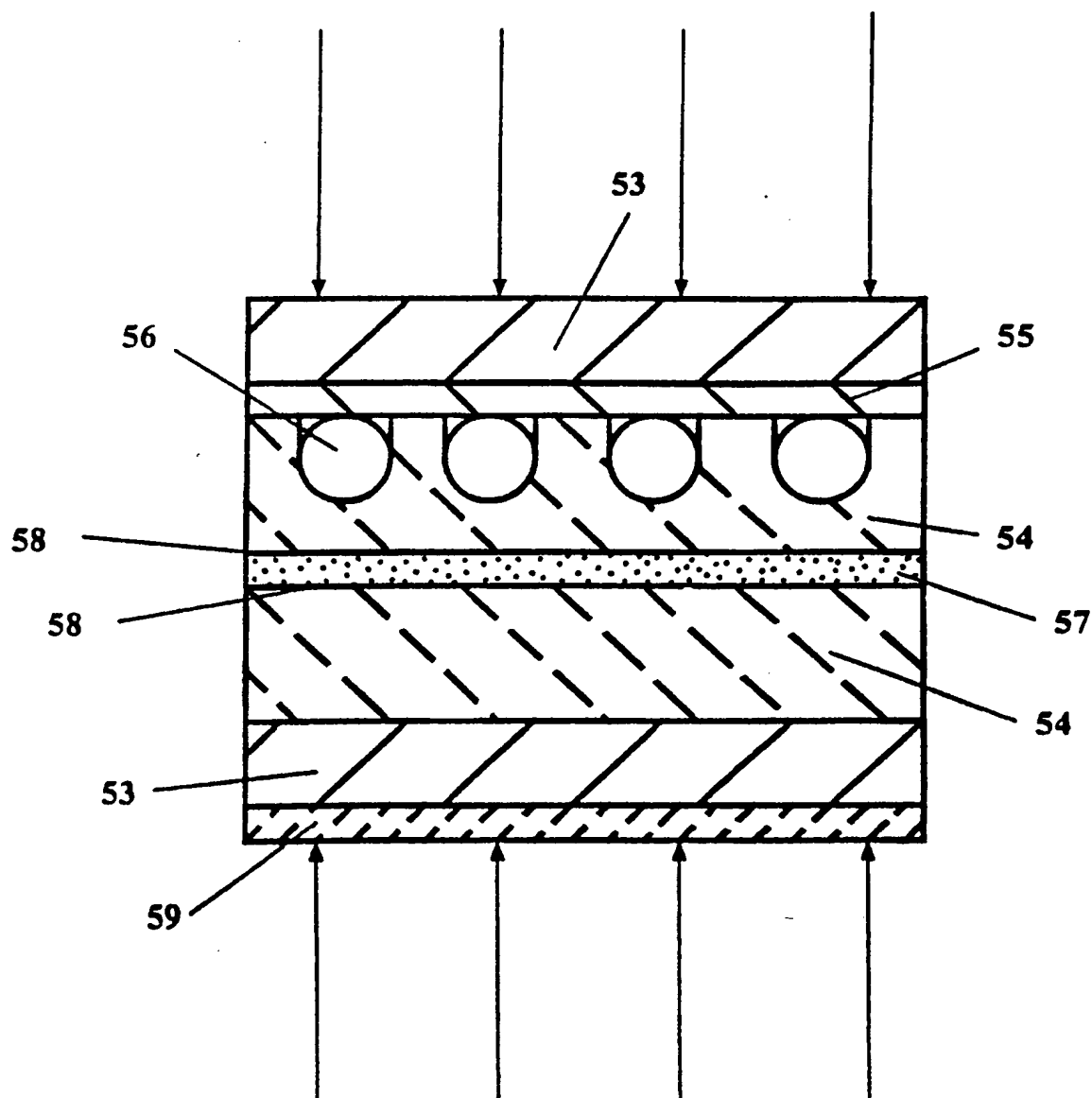


FIG. 16

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/14913

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B32B 3/00, 15/00; B21F; H01L 29/12

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/210, 209, 433, 539.5, 615, 620, 901  
427/229

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,155,665 A (KOMORITA et al) 13 October 1992, column 4, lines 45-50.	1-50
X	US 5,153,077 A (KASHIBA et al) 06 October 1992, column 1, lines 25-29, and column 3, lines 18-25.	1-50
X	US 4,959,507 A (TANAKA et al) 25 September 1990, column 1, lines 53-56, and column 5, lines 7-10.	1-50

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 NOVEMBER 1997

Date of mailing of the international search report

12 DEC 1997

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**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US97/14913

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,318,800 A (GONG et al) 07 June 1994, column 2, lines 31-38.	1-50

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US97/14913

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

428/210, 209, 433, 539.5, 615, 620, 901

427/229

3-94

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